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SULFUR RECOVERY FROM FLUE GAS
VIA
REVERSIBLE DRY ABSORBENT

Contract No. PH 22-68-40

with

U. S. Department of Health, Education, and Welfare
Consumer Protection and Environmental Health Service
National Air Pollution Control Administration

SUMMARY REPORT

June 20, 1968 to June 19, 1969

Callery Chemical Company
Division of Mine Safety Appliance Company
Callery, Pennsylvania 16024

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16. Abstracts The feasibility was studied of a process for removal of sulfur oxides from flue gas using a reversible dry absorbent. Sulfur dioxide in the flue gas is first oxidized to SO3 and then absorbed on a fluidized solid. The sorbent consists of Na_2SO_4 impregnated on an inert carrier and takes up SO3 through the formation of sodium pyrosulfate. Oxidation of SO2 was not studied, however, catalytic oxidation was used to prepare an SO3 feed stream for the experimental program. An experimental program was carried out to develop kinetic and equilibrium data for the reaction of Na_2SO_4 supported on silica gel with SO3. The data were obtained under conditions suitable for a cyclic absorption and desorption process. Using a silica carrier impregnated with about 20% Na_2SO_4, absorption of SO3 from simulated flue gas was found to be rapid in the temperature range of 545 F to 600 F. The absorption rate was constant up to about 70% of sorbent capacity, with no indication of pore diffusional resistance. The equilibrium SO3 pressure at 545 F was found to be low enough to permit removal of over 95% of the SO3 which would result from oxidation of the SO2 in flue gas. Nitrogen oxides and water vapor in the concentration normally found in flue gas were found to have little effect on the SO3 absorption rate. Desorption of SO3 at a concentration of 6% in the gas was found to be very rapid at 930 F, and essentially quantitative

(continued on back of page)

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recovery of SO3 was obtained at 1020 F. A process design was developed based on the reaction rates and temperature conditions determined in the experimental program. Economic studies pointed up the importance of using an inexpensive catalyst and sorbent and minimizing the loss of these materials. Therefore, the concept of using a combined catalyst and sorbent consisting of fly ash impregnated with V2O5 and Na2SO4 was developed. Preliminary experiments carried out using a fly ash based catalyst and fly ash sorbent were promising. The desorbed SO3 can be absorbed in sulfuric acid to produce concentrated H2SO4 or oleum for sale, or by maintaining a slightly reducing atmosphere in the desorber, a concentrated stream of SO2 (44%) can be produced. ~~Capital and operating costs for recovery of sulfur oxides from flue gas were estimated, with the results shown in Table I.~~ The estimated capital and operating costs show that the process is competitive with alternative processes. In areas where a market for concentrated sulfuric acid or oleum exists the process would be especially attractive, and it is believed that a profitable recovery situation could be developed. Potential advantages over alternative processes result from the use of a low cost fly ash sorbent and from the relatively low regeneration temperature, which minimizes corrosion problems.

CCC 69-31

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SUMMARY REPORT

June 20, 1968 to June 19, 1969

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CCC 69-31

SUMMARY

Under Contract PH 22-68-40, a feasibility study was carried out by Callery Chemical Company on a process for removal of sulfur oxides from flue gas using a reversible dry absorbent.

The process concept is illustrated in Figure 1. Sulfur dioxide in the flue gas is first oxidized to SO_3 and then absorbed on a fluidized solid. The sorbent consists of Na_2SO_4 impregnated on an inert carrier and takes up SO_3 through the formation of sodium pyrosulfate in accordance with the following equation:

$$Na_2SO_4 + SO_3 \rightleftharpoons Na_2S_2O_7$$

A study of the oxidation of SO_2 was not included in the Callery program; however, catalytic oxidation was used to prepare an SO_3 feed stream for the experimental program.

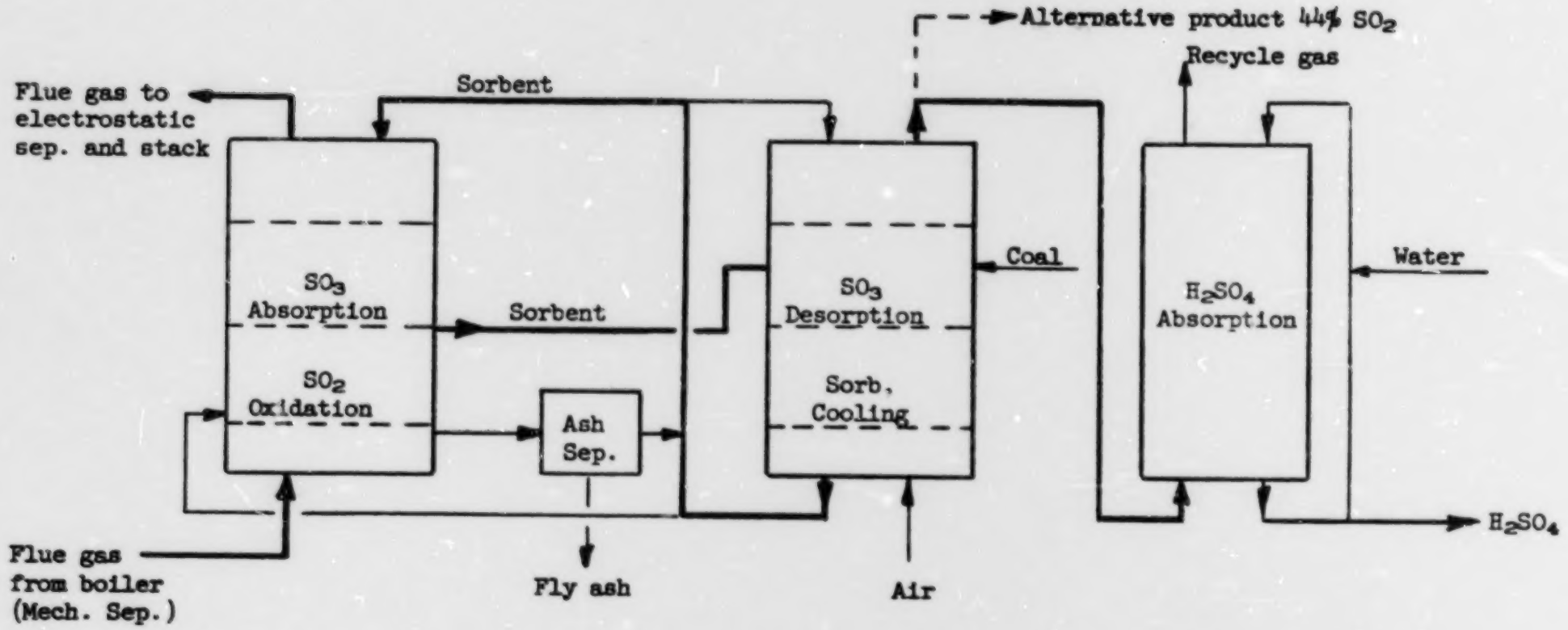
An experimental program was carried out to develop kinetic and equilibrium data for the reaction of Na_2SO_4 supported on silica gel with SO_3. The data were obtained under conditions suitable for a cyclic absorption and desorption process.

Using a silica carrier impregnated with about 20% Na_2SO_4, absorption of SO_3 from simulated flue gas was found to be rapid in the temperature range of 545°F to 600°F. The absorption rate was constant up to about 70% of sorbent capacity, with no indication of pore

CCC 69-31

FIGURE 1

BASIC PROCESS FLOW DIAGRAM



diffusional resistance. The equilibrium SO_3 pressure at 545°F was found to be low enough to permit removal of over 95% of the SO_3 which would result from oxidation of the SO_2 in flue gas. Nitrogen oxides and water vapor in the concentration normally found in flue gas were found to have little effect on the SO_3 absorption rate.

Desorption of SO_3 at a concentration of 6% in the gas was found to be very rapid at 930°F, and essentially quantitative recovery of SO_3 was obtained at 1020°F.

A process design was developed based on the reaction rates and temperature conditions determined in the experimental program. Economic studies pointed up the importance of using an inexpensive catalyst and sorbent and minimizing the loss of these materials. Therefore, the concept of using a combined catalyst and sorbent consisting of fly ash impregnated with V_2O_5 and Na_2SO_4 was developed. Preliminary experiments carried out using a fly ash based catalyst and fly ash sorbent were promising; however, time did not permit carrying these experiments to conclusive data, and the combination catalyst-sorbent was not investigated.

As shown in Figure 1, the desorbed SO_3 can be absorbed in sulfuric acid to produce concentrated H_2SO_4 or oleum for sale, or by maintaining a slightly reducing atmosphere in the desorber, a concentrated stream of SO_2 (44%) can be produced. Capital and operating costs for recovery of sulfur oxides from flue gas were estimated with the results shown in Table I.

CCC 69-31

TABLE I

CAPITAL AND OPERATING COST SUMMARY

1400 MW Power Plant, 0.2% SO_2 in Flue Gas
Operating 330 days/year at 70% Capacity

	Concentration of SO_2 to 44%	Sulfuric Acid Production
Capital Investment,	$ 7,880,000	$ 10,220,000
$/KW	5.63	7.3
Operating Cost, $/year	2,590,000	3,250,000
$/ton coal	0.81	1.01
Mil/kwh	0.33	0.42
Break even acid sales price, $/ton H_2SO_4	---	17.80

CCC 69-31

CONCLUSIONS AND RECOMMENDATIONS

It has been demonstrated that the reaction of SO_3 with Na_2SO_4 supported on a carrier is rapid and quantitatively reversible, and that the equilibrium pressure of SO_3 increases sharply with temperature in a range well suited to a cyclic process for recovering sulfur oxides from flue gas. The estimated capital and operating costs, summarized in Table I, show that the process is competitive with alternative processes now being considered.

In areas where a market for concentrated sulfuric acid or oleum exists the process would be especially attractive, and it is believed that a profitable recovery situation could be developed.

Potential advantages over alternative processes result from the use of a low cost fly ash sorbent and from the relatively low regeneration temperature, which minimizes corrosion problems.

Further study is recommended to develop a sorbent, based on fly ash impregnated with V_2O_5 and Na_2SO_4, which is suitable both for oxidation of SO_2 and for absorption of SO_3, and will have physical properties suitable for large scale gas-solid contacting.

CCC 69-31

TABLE OF CONTENTS

	Page
SUMMARY	1
CONCLUSIONS AND RECOMMENDATIONS	5
TABLE OF CONTENTS	6
List of Illustrations	6a
List of Tables	6b
I. INTRODUCTION	7
II. EXPERIMENTAL PROGRAM	9
A. Objectives and Approach	9
B. Apparatus	10
C. Procedure	14
D. Results	17
1. Sorbent Preparation	17
2. Absorption of SO_3	19
a. Effect of sorbent size and gas velocity	19
b. Effect of water vapor	23
c. Effect of nitrogen oxides	25
d. Effect of temperature	28
e. Effect of Na_2SO_4 conversion	30
f. Effect of fly ash substrate	34
3. Desorption of SO_3	38
4. Fly Ash Catalyst	41
III. ECONOMIC EVALUATION	43
A. Description of Process	43
1. Sulfuric Acid Production	43
2. Concentration of SO_2	45
B. Special Features	47
C. Cost Summary	48
D. Catalyst-sorbent	48
E. Converter-absorber	50
1. Description of Contactor	50
2. Depth of Sorbent Required	52
F. Desorber	55
1. Sulfuric Acid Production	55
2. Concentration of SO_2	58
G. SO_3 Absorber	58
H. Cost Estimates	59
IV. APPENDIX	63

CCC 69-31

TABLE OF CONTENTS (continued)

LIST OF ILLUSTRATIONS

Figure		Page
1.	BASIC PROCESS FLOW DIAGRAM	2
2.	SCHEMATIC DIAGRAM OF APPARATUS	11
3.	DETAIL OF SAMPLE AREA	13
4.	SCHEMATIC OF REACTOR AREA FOR WATER VAPOR ADDITION	15
5.	SO_3 ABSORPTION CURVES	21
6.	EFFECT OF WATER VAPOR	24
7.	EFFECT OF NITROGEN OXIDES	26
8.	EFFECT OF EQUILIBRIUM SO_3 PRESSURE	29
9.	EQUILIBRIUM STUDIES	31
10.	EQUILIBRIUM STUDIES	32
11.	ABSORPTION STUDIES AT LOW SO_3 CONCENTRATION	33
12.	SO_3 ABSORPTION BY FLY ASH	36
13.	SO_3 DESORPTION FROM FLY ASH	37
14.	DESORPTION OF SO_3 AT 500°C to 605°C	39
15.	DESORPTION OF SO_3 AT 550°C	40
16.	FLOW SHEET - H_2SO_4 PRODUCTION	44
17.	FLOW SHEET - SO_2 CONCENTRATION	46
18.	CONVERTER-ABSORBER	51a
19.	DECOMPOSITION PRESSURE $Na_2S_2O_7$	53
20.	SO_3 DESORBER	56

CCC 69-31

TABLE OF CONTENTS (continued)

LIST OF TABLES

Table		Page
I	CAPITAL AND OPERATING COST SUMMARY	4
II	SORBENT PREPARATION DATA	18
III	EXPERIMENTAL CONDITIONS AND RESULTS	22
IV	EXTENT OF Na_2SO_4 CONVERSION AT 330°C	23
V	EXPERIMENTAL RESULTS, RUNS 5A-6, 7A-5 and 6	27
VI	EFFECT OF TEMPERATURE ON ABSORPTION RATE	28
VII	Na_2SO_4 CONVERSION ON SILICA AND FLY ASH	35
VIII	SO_3 RELEASE RATE AT VARIOUS TEMPERATURES	38
IX	MATERIAL BALANCE, SO_3 ABSORPTION-DESORPTION	41
X	CAPITAL INVESTMENT, SULFURIC ACID PRODUCTION	59
XI	CAPITAL INVESTMENT, CONCENTRATION OF SO_2 TO 44%	60
XII	OPERATING COST, SULFURIC ACID PRODUCTION	61
XIII	OPERATING COST, CONCENTRATION OF SO_2 TO 44%	62
XIV	EXPERIMENTAL DATA	63

CCC 69-31

I. INTRODUCTION

Callery Chemical Company is developing a process for the removal of sulfur oxides from flue gas under Contract PH 22-68-40 with the U. S. Department of Health, Education, and Welfare, National Air Pollution Control Administration. This report summarizes the work carried out during the contract period, June 20, 1968 to June 19, 1969.

The process is based on the use of a dry absorbent which will catalyze the oxidation of SO_2 to SO_3, and absorb the SO_3 from the gas stream. The catalyst-sorbent, which consists of Na_2SO_4 and V_2O_5 impregnated on a silica substrate, absorbs SO_3 via the formation of sodium pyrosulfate in accordance with the following equation:

$$Na_2SO_4 + SO_3 \longrightarrow Na_2S_2O_7$$

The catalyst-sorbent is regenerated by heating, and the sulfur oxides recovered either in the form of concentrated sulfuric acid or as a concentrated stream of SO_2 gas suitable for reduction to sulfur.

The novel process concept was initially developed in an engineering study carried out and funded by Callery Chemical Company. This study was based on experimental work previously carried out for Callery by Bjorksten Research Laboratories [1] and on calculated equilibrium data.

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(1) Report No. CCC-1024-TR-14, Pyrolysis of Sodium Pyrosulfate, Bjorksten Research Laboratories, 3/25/54.

The catalytic oxidation of SO_2 to SO_3 is being studied by others, and investigation of this part of the process was not included in the Callery program. Callery utilized this reaction in the experimental program as means of obtaining a stream of SO_3 of known concentration, and a preliminary experiment was carried out to show the feasibility of the combined catalyst-sorbent concept.

CCC 69-31

II. EXPERIMENTAL PROGRAM

A. Objectives and Approach

The objectives of the experimental program were to,

- demonstrate the reversible reaction of SO_3 with sodium sulfate impregnated on a silica-alumina support
- determine equilibrium and rate data, and absorption capacity under conditions suitable for a continuous process for removing SO_2 from flue gas
- determine the effects of other flue gas components
- consider the use of sulfates other than Na_2SO_4.

Sulfates other than Na_2SO_4 were not investigated experimentally because the relatively inexpensive sodium sulfate was found to be satisfactory. Potassium sulfate reacts with SO_3 to form a pyrosulfate; however, the lower melting point and higher decomposition temperature of $K_2S_2O_7$ make this reaction less suitable for the process. Calcium and iron sulfates do not react with SO_3 under the process conditions.

The absorption and desorption phases of the program were studied concurrently. Two methods were tried. The first, which was unsuccessful, consisted of following the rate of absorption of SO_3 by the Na_2SO_4 indirectly by monitoring the unabsorbed SO_3. This was accomplished by scrubbing the effluent from the reactor over set time intervals and calculating the difference from established feed rates. This technique had two basic

CCC 69-31

problems. In spite of considerable effort we were never able to establish a consistently accurate method of feeding gaseous SO_3 into the diluent nitrogen, and the effluent scrubbing technique made it necessary to make long experimental runs with large samples in order to get enough data points.

The second method worked exceptionally well. The SO_3 takeup was measured directly by weight gain of the sample. The feed stream was prepared by passing a pre-set SO_2-N_2 mixture and oxygen through a catalytic converter to produce SO_3. The resultant stream was passed through a bed of the Na_2SO_4-impregnated silica, and the sample periodically weighed. The release of SO_3 was followed in the same manner.

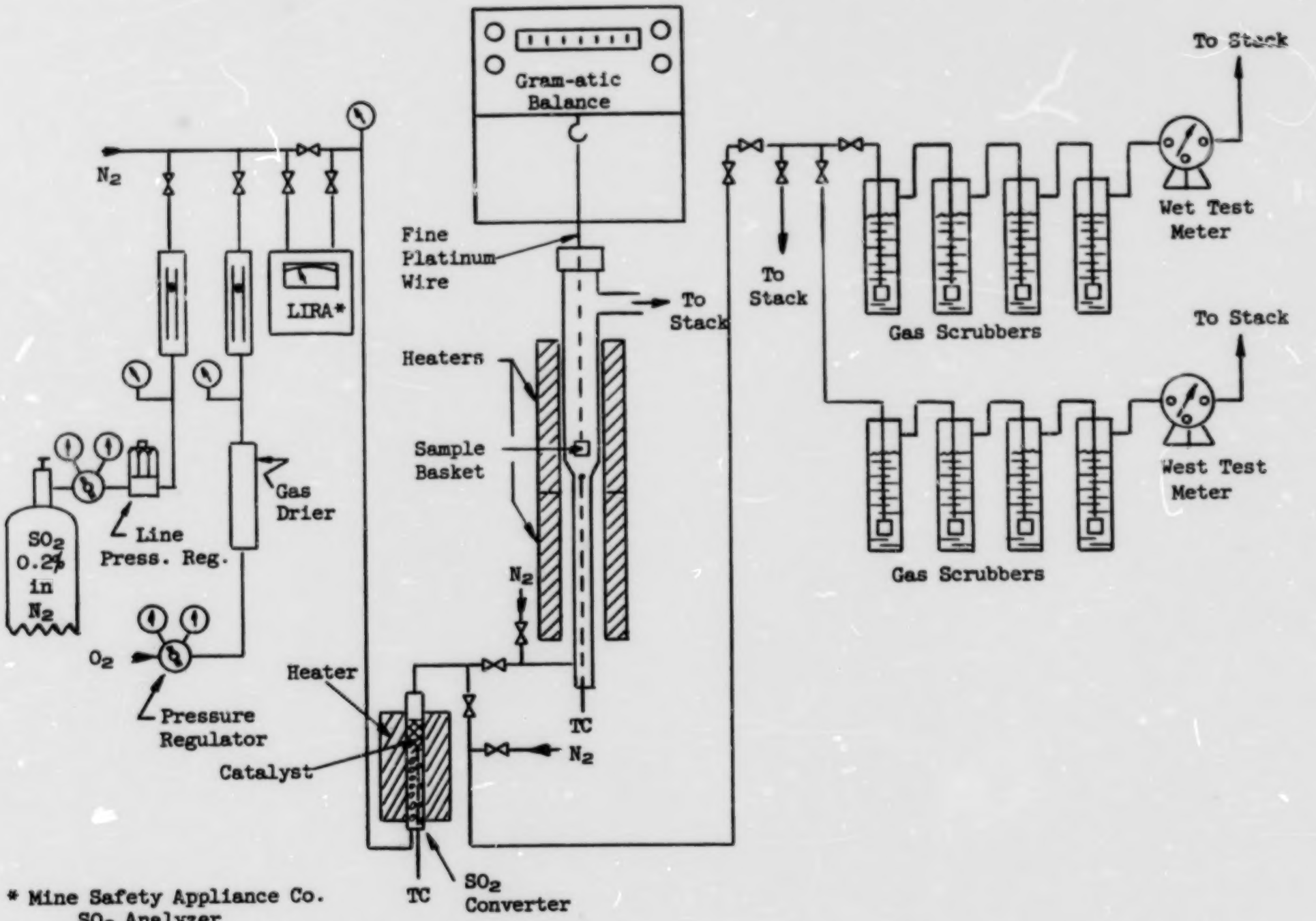
This second method was the source of all the rate data developed for the program for both the absorption and desorption phases. The apparatus and technique for this method, therefore, will be covered in detail.

B. Apparatus

A sketch of the apparatus for following the absorption and desorption of SO_3 by the sorbent is shown schematically in Figure 2. The basic construction was stainless steel except for the scrubber area, where glass was employed. Globe valves were used except for gas metering where one degree angle stainless steel metering valves were employed. The reactor, sample holder and converter were all of stainless steel construction.

The basic SO_2 feed stock was purchased from Scientific Gas Products, Inc. Two feed stocks were used. One contained 2050 ppm SO_2 in

FIGURE 2
SCHEMATIC DIAGRAM OF APPARATUS



* Mine Safety Appliance Co.
SO_2 Analyzer

CCC 69-31

nitrogen. The other contained 3100 ppm SO_2 and 500 ppm NO in nitrogen. Oxygen for the conversion of SO_2 to SO_3 was added to the stream after first having been dried through a bed of 13X molecular sieve. Rotameters were used to monitor all gas streams.

The converter for SO_2 oxidation consisted of an 18 inch section of one inch O.D. stainless steel tube packed about one-half full of stainless steel Raschig rings for heat transfer, and containing about 20 grams of Harshaw K_2O-activated V_2O_5 catalyst. The converter was controlled at 450°C with a tube furnace during operation.

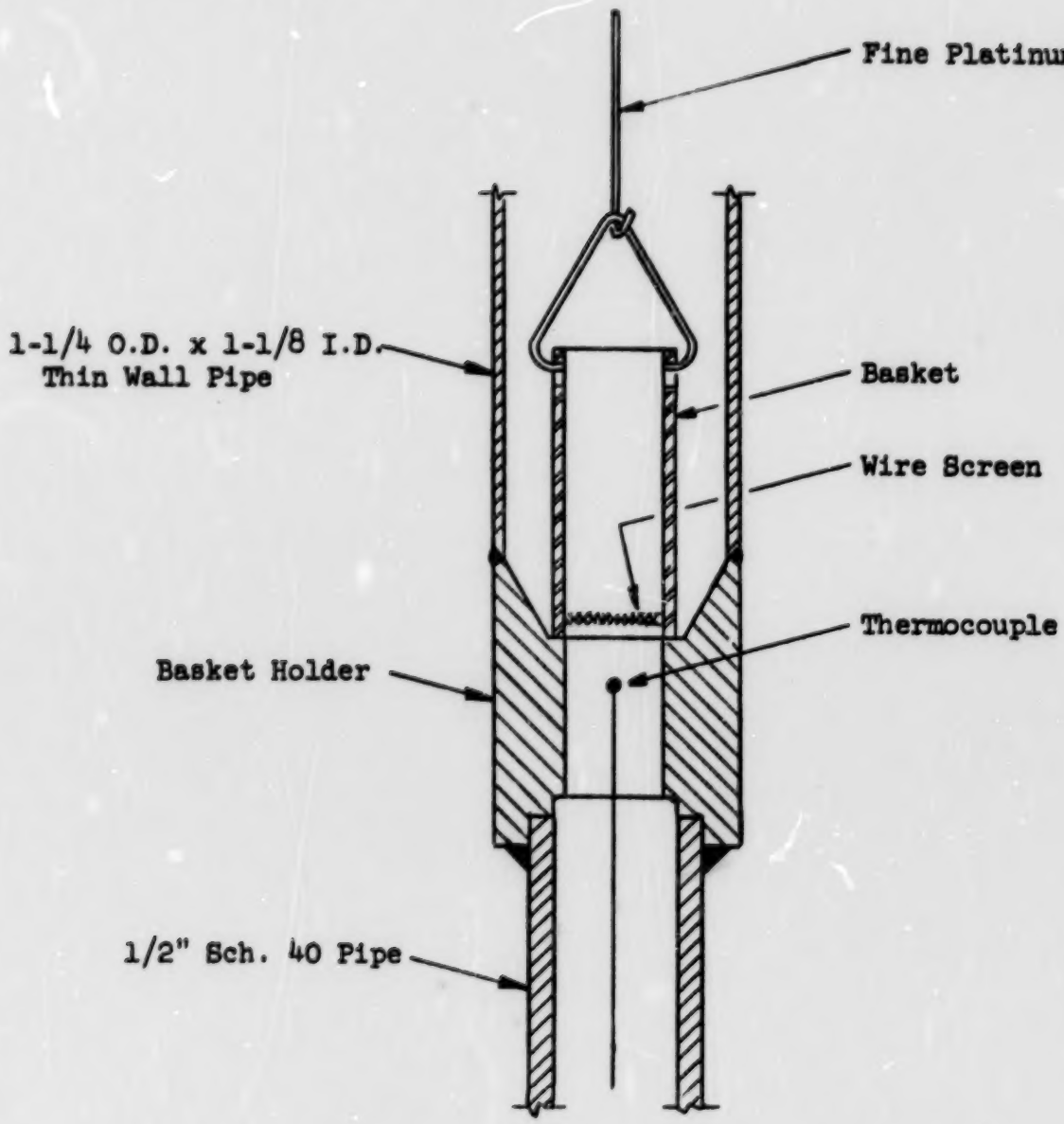
The reactor was constructed of a 22 inch section of 1/2 inch schedule 40 stainless pipe and a 16 inch section of 1-1/4 inch O.D. thin-wall stainless pipe welded together at the basket holder. The 1/2 inch Schedule 40 pipe served as a preheat area for the feed stream. The 1-1/4 inch O.D. pipe allowed for insertion of sample holder and contact-free weighing.

Detail of the sample area is shown in Figure 3. The sample basket consisted of a short length of one-half inch stainless tubing with a stainless steel screen base, and was attached by a fine platinum wire which passed through a threaded cap to a modified Mettler balance. The basket was suspended from the balance during weighings, but when in the absorption or desorption phase, it was at rest on the basket holder. The basket holder was constructed so that the sample basket, when at rest, would completely cover the reagent gas opening. All of the reagent or sweep gas, therefore,

CCC 69-31

FIGURE 3

DETAIL OF SAMPLE AREA - FULL SCALE



CCC 69-31

has to pass through the sample bed. A thermocouple monitored the reagent gas temperature at a point about one cm below the basket. This value was considered to be the sample temperature.

The reactor area was modified as shown in Figure 4 to introduce water vapor into the feed stream. Nitrogen, at a rate of 115 cc/min was passed through water held at 77°C, and this mixture introduced into the SO_3-N_2 stream at a point about 4 inches into the preheat zone, and about 10 inches below the sample. Lines from the converter and the water vapor source were heated to prevent condensation.

The gas scrubbers were two banks of four glass traps equipped with medium fritt gas dispersers. The base sections were removable for easy replacement of scrubbing solution and were approximately 250 cc in volume.

C. Procedure

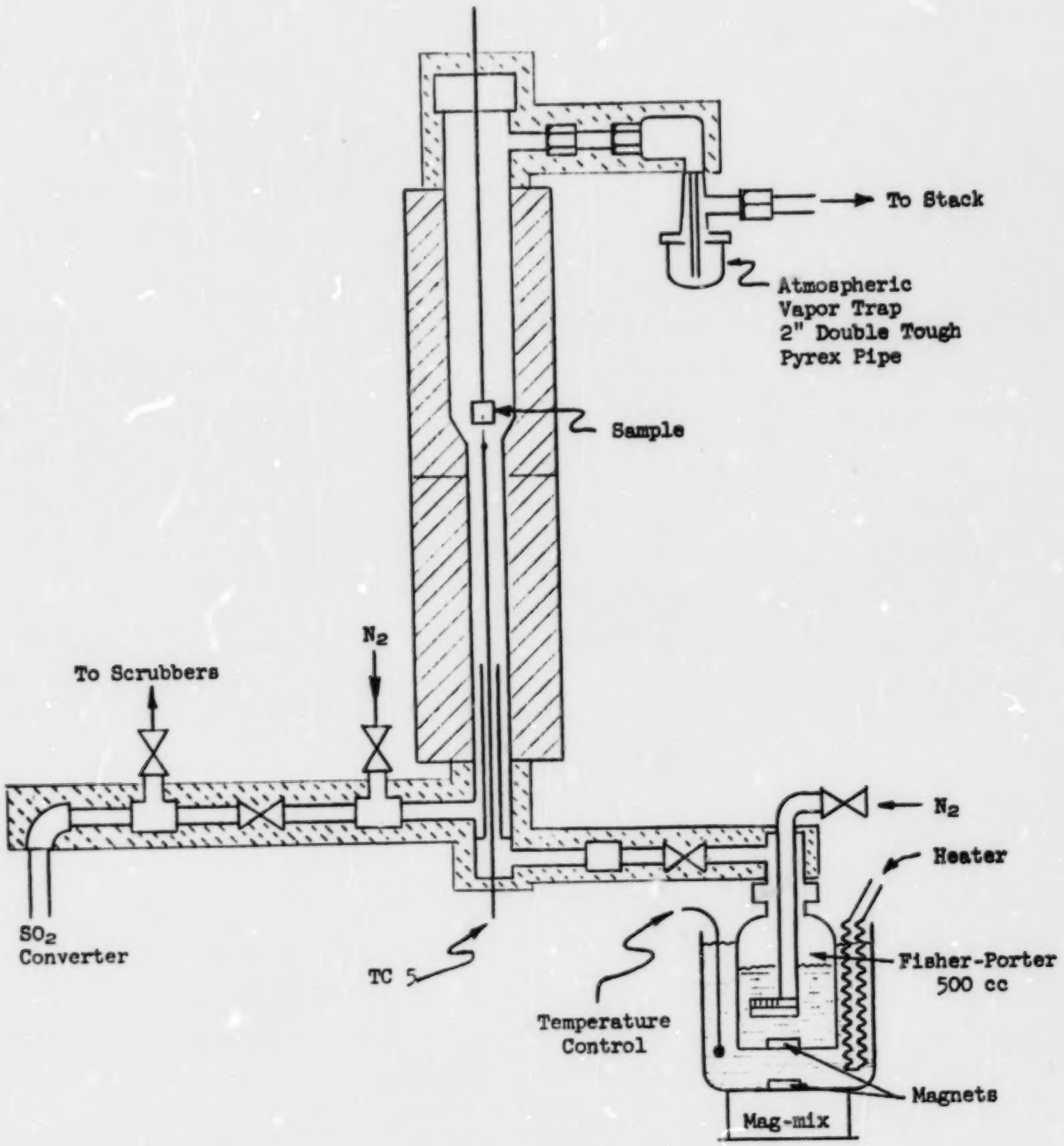
The general procedure for following the absorption of SO_3 on the sorbent was as follows: A known weight of sorbent containing Na_2SO_4 was charged into the sample holder and lowered into the reactor to the rest position. The sample sizes and weights varied. In the initial experiments using the direct weight method, sample weights of about 1.8 g of 3 to 8 mesh material were used. In later experiments, 0.4 g samples of 10 to 16 mesh material were employed.

The sample was heated to the desired temperature and swept with

CCC 69-31

FIGURE 4

SCHEMATIC OF REACTOR AREA FOR WATER VAPOR ADDITION



CCC 69-31

dry nitrogen to constant weight. While this was in progress, the converter efficiency was measured by passing the feed stock and oxygen (ca 2 mole percent) through the converter and passing the effluent through the scrubbers for a set period of time. The first two scrubbers contained 150 mls of a 20% water-in isopropanol solution to remove SO_3 as H_2SO_4. The third scrubber contained 150 ml of a 0.02N iodine solution to measure unconverted SO_2, and the fourth a $Na_2S_2O_3$ solution to catch iodine swept over from the third trap. The conversion efficiency was taken as the amount of SO_3 produced as measured by acid content of traps one and two ($SO_3 \cong 2H^+$) divided by the total SO_2 charged, as calculated from the flow rate and SO_2 feed stock concentration. The unconverted SO_2 value from traps three and four were used as a check on the total SO_2 fed.

Immediately following the converter efficiency determination the sample stream was passed through the heated sample at 930-940 cc/min. At intervals, the sample flow was diverted to the stack, and the sample suspended from the balance and weighed. At the conclusion of the run the SO_3 converter efficiency was again measured.

Desorption was carried out similarly, using only nitrogen as a sweep gas at 200 cc/min. The loaded sorbent sample was rapidly heated to the desired desorption temperature and the nitrogen passed through the bed to sweep out SO_3 released. Again, the sweep gas was periodically diverted and the charge weighed to determine weight loss.

CCC 69-31

D. Results

1. Sorbent Preparation

Initial sorbent studies were limited to the preparation of a sorbent which would be representative and readily duplicated for use in studying the process variables. Three carrier samples were furnished by the Davison Chemical Division, W. R. Grace and Company, and were identified as follows:

Silica Gel, grade 59 (3 - 8 mesh)

Grade 542 beads

Silica alumina, grade 979 (3/16 inch pellets)

Sorbents were prepared by impregnating these carriers with Na_2SO_4 dissolved in water. Impregnated samples were filtered and dried at 120°C for 16 hours. Drying times greater than 16 hours at 120°C did not result in further weight loss.

The results of initial experiments are shown in Table II. In series B through E, the carriers were first washed with distilled water, then dried at 120°C prior to being placed in the impregnating solution. In series C, the carriers were evacuated for one hour prior to addition of the solution to the evacuated reactor. In series D and E, the carriers were added to the boiling saturated solution, boiled for 15 minutes, then cooled to ambient temperature for the period shown and dried.

It was found that impregnation in the range of 20% by weight of Na_2SO_4 could be achieved simply using a 2.8N Na_2SO_4 solution at 30°C with

TABLE II

SORBENT PREPARATION DATA

Series	Carrier	Impregnating Solution (conc. of Na_2SO_4)	Carrier Preparation	Impregnating Conditions: Sol'n Temp. (°C)	Impregnating Conditions: Immersion Time (hours)	Weight Gain per gram Carrier	Weight % Na_2SO_4
B	Silica Gel (59)	2.8 N	washed, dried at 120°	30	4	.25	19
	Beads (542)	2.8 N		30	4	.10	9.2
	Pellets (979)	2.8 N		30	4	.20	16.5
C	Silica Gel (59)	2.8 N	washed, dried at 120° evacuated	30	2	.14	12
	Beads (542)	2.8 N		30	2	.029	2.8
	Pellets (979)	2.8 N		30	2	.20	17
D	Beads (542)	sat.	washed, dried at 120°	100-30	.25 - 2	.09	8.5
	Pellets (979)	sat.		100-30	.25 - 2	.26	21
E	Silica Gel (59)	sat.	washed, dried at 120°	100-30	.25 - 20	.21	17.5
	Beads (542)	sat.		100-30	.25 - 20	.06	5.5
	Pellets (979)	sat.		100-30	.25 - 20	.21	17

	Bulk Density g/cc*
Silica Gel (59)	0.32
Beads (542)	0.54
Pellets (979)	0.34

* Bulk density measured in 1/2" ID tube

CCC 69-31

either the silica gel or the silica alumina. Silica gel sorbent was selected for the experimental program.

It was hoped that other substrates could be investigated based on the results of experimental and economics studies. However, only a preliminary experiment using fly ash substrate was possible within the contract period.

2. Absorption of SO_3

a. Effect of sorbent size and gas velocity

Typical data for the absorption of SO_3 on Na_2SO_4 sorbent are plotted on Figure 5. The experiments are identified by a 3-character run number. The first number indicates the sorbent charge; the letter A or D indicates absorption or desorption, and the last number indicates the cycle for the particular charge. Thus, run number 2A-3 is the third absorption step for sorbent charge number 2.

Initial experiments using the direct weight method were run with a 0.5 inch diameter reactor and a sample weight of about 1.7 grams. The 2A absorption series is representative of this operation, and the experimental conditions and results are listed in Table 3 for run 2A-4. Absorption of SO_3 in this series is limited because the SO_3 concentration in the outlet gas is essentially in equilibrium with the SO_3 pressure over $Na_2S_2O_7$.

In order to reduce the amount of SO_3 absorbed, the 0.5 inch

CCC 69-31

reactor was replaced with a 0.25 inch diameter reactor and the sorbent charge reduced to about 0.4 grams while maintaining the same gas flow. The sorbent size was reduced to 10-16 mesh for use in the smaller reactor. Run 6A-2 is representative of this condition, and the results are plotted on Figure 5 and listed in Table III for comparison with Run 2A-4.

Using the smaller diameter reactor, the absorption rate was essentially constant up to 67% of the capacity of the sorbent, and during this constant rate period, about 40% of the SO_3 fed was absorbed. As a result of the higher mass velocity of the gas, the calculated drop in SO_3 pressure from gas phase to particle surface was reduced by about 60%, when compared with run 2A-4.

Absorption rates have been correlated based on a driving force equal to the difference between the average SO_3 pressure and the equilibrium SO_3 pressure, (Y-Ye). Thus, the absorption rate constant,

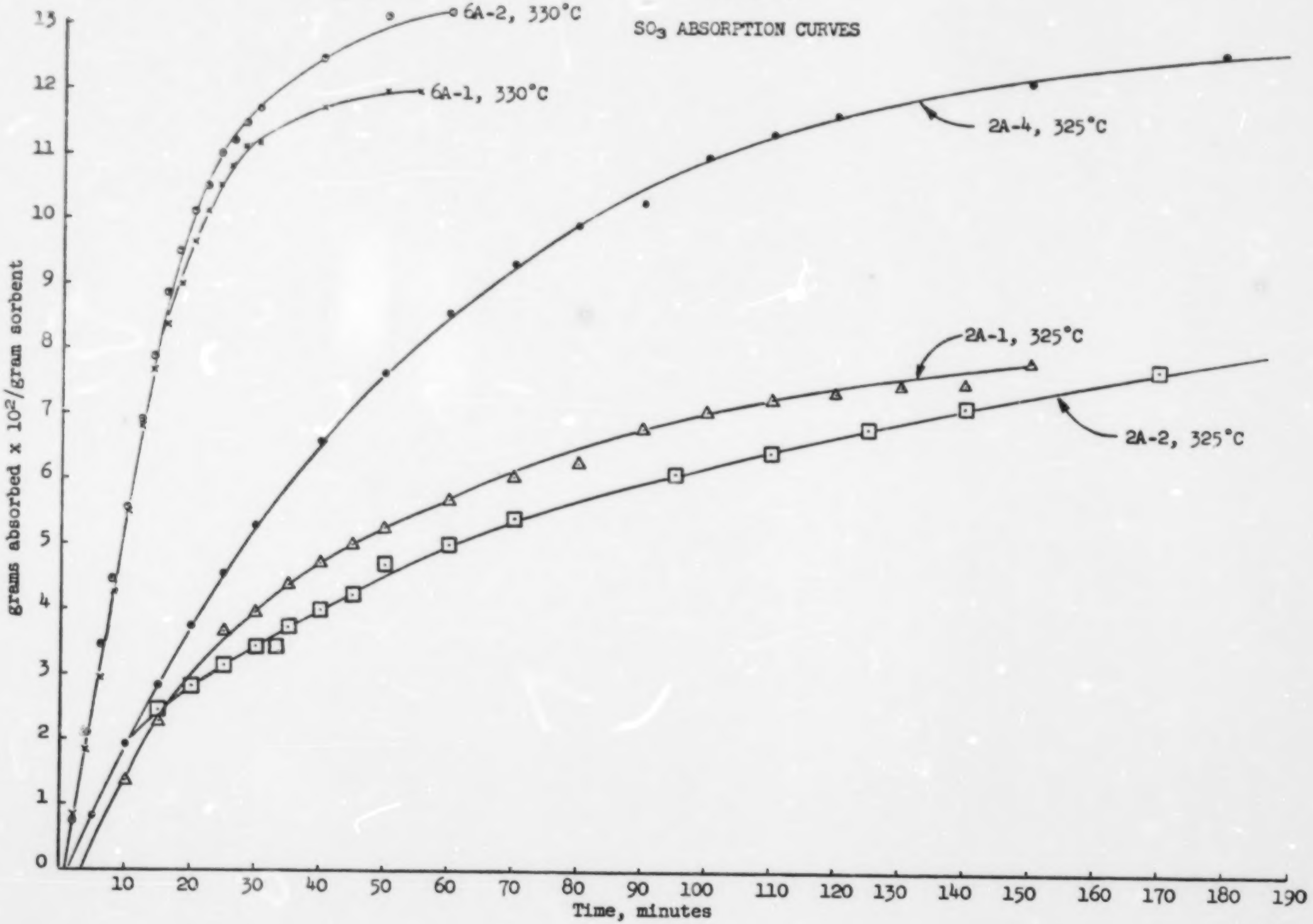
$$k = \frac{\text{lbs } SO_3 \text{ absorbed}}{\text{hour x lb sorbent x (Y-Ye)}}$$

For this evaluation it was assumed that the absorption rate was constant throughout the operating range of sorbent capacity; that is, that the rate did not vary with the extent of Na_2SO_4 conversion to $Na_2S_2O_7$. However, there is some evidence (discussed in Section e) that a solid solution is formed; and that the equilibrium SO_3 pressure varies with the extent of Na_2SO_4 conversion. This small effect is masked in runs such as 6A-2 in which the SO_3 pressure in the gas is appreciably higher than equilibrium.

CCC 69-31

FIGURE 5

SO_3 ABSORPTION CURVES



CCC 69-31

TABLE III

EXPERIMENTAL CONDITIONS AND RESULTS

Run No.	2A-4	6A-2
Temperature, °C	330	330
Sorbent size, mesh	3-8	10-16
Sorbent weight, grams	1.7396	0.4060
Weight % Na_2SO_4 in sorbent	25	25
Gas composition, SO_2, ppm (InN_2)	2050	2050
Gas flow, $cm^3/min.$	930	930
Oxygen flow, $cm^3/min.$	20	20
SO_2 conversion to SO_3, before, %	77	81.9
SO_2 conversion to SO_3, after, %	49	--
Na_2SO_4 reacted with SO_3, %	89.9	93.1
Sorbent bed height, inches	1.68	1.57
Sorbent bed diameter, inches	0.5	0.25
Gas contact time at temp., sec.	0.16	0.037
Gas velocity, ft/sec.	0.40	3.54
N_{Re}, Reynolds No.	16	30
N_{Sch}, Schmidt No.	1.85	1.85
G, Mass velocity, lbs/hr x ft^2	112	450
Calc, mass transfer rate, gas to sorbent surface $kg = J_D \times G/80 \times N_{Sch}^{2/3}$, lb moles/hr x ft^2 x atmos	0.418	1.04
Outside surface of sorbent, ft^2	0.082	0.034
Calc transfer rate, gas to sorbent, lb moles/hr x atm	0.0343	0.0356
Range of constant absorption rate, % of capacity	0-41	0-67
Constant absorption rate, lbs SO_3/hr x lb sorb.	0.106	0.334
SO_3 absorbed from gas (constant rate period) % of SO_3 fed	67	40
ΔP, gas to sorbent, atmos	0.016×10^{-2}	1×10^{-4}
Inlet SO_3 pressure at sorbent surface, atmos	0.00113	0.00158
Outlet SO_3 pressure at sorbent surface, atmos	0.00027	0.00090
Average SO_3 pressure at sorbent surface, atmos	0.00070	0.00124
Equilibrium SO_3 pressure at 330°C	0.00034	0.00034
Absorption rate constant k = lbs SO_3 abs/hr x lb sorb x (Y-Ye)	295	372

CCC 69-31

The calculated absorption rate constants as shown in Table III are 295 and 372 for runs 2A-4 and 6A-2 respectively. Since a correction was made for the effect of increased mass velocity, the increase results from the smaller particle size and from improved experimental accuracy obtained through reduced SO_3 absorption.

A comparison of the percent conversion of Na_2SO_4 to $Na_2S_2O_7$ is shown in Table IV.

TABLE IV

EXTENT OF Na_2SO_4 CONVERSION AT 330°C

Run No.	Mesh Size of Sample	Na_2SO_4 Converted %
2A-1	3-8	55.8
2A-2	3-8	66.7
2A-3	3-8	84.6
2A-4	3-8	89.9
5A-1	10-16	89.1
6A-1	10-16	85.0
6A-2	10-16	93.1

The reason for increased absorption in subsequent runs in the 2A series is not known, but the change is minor in the 6A series.

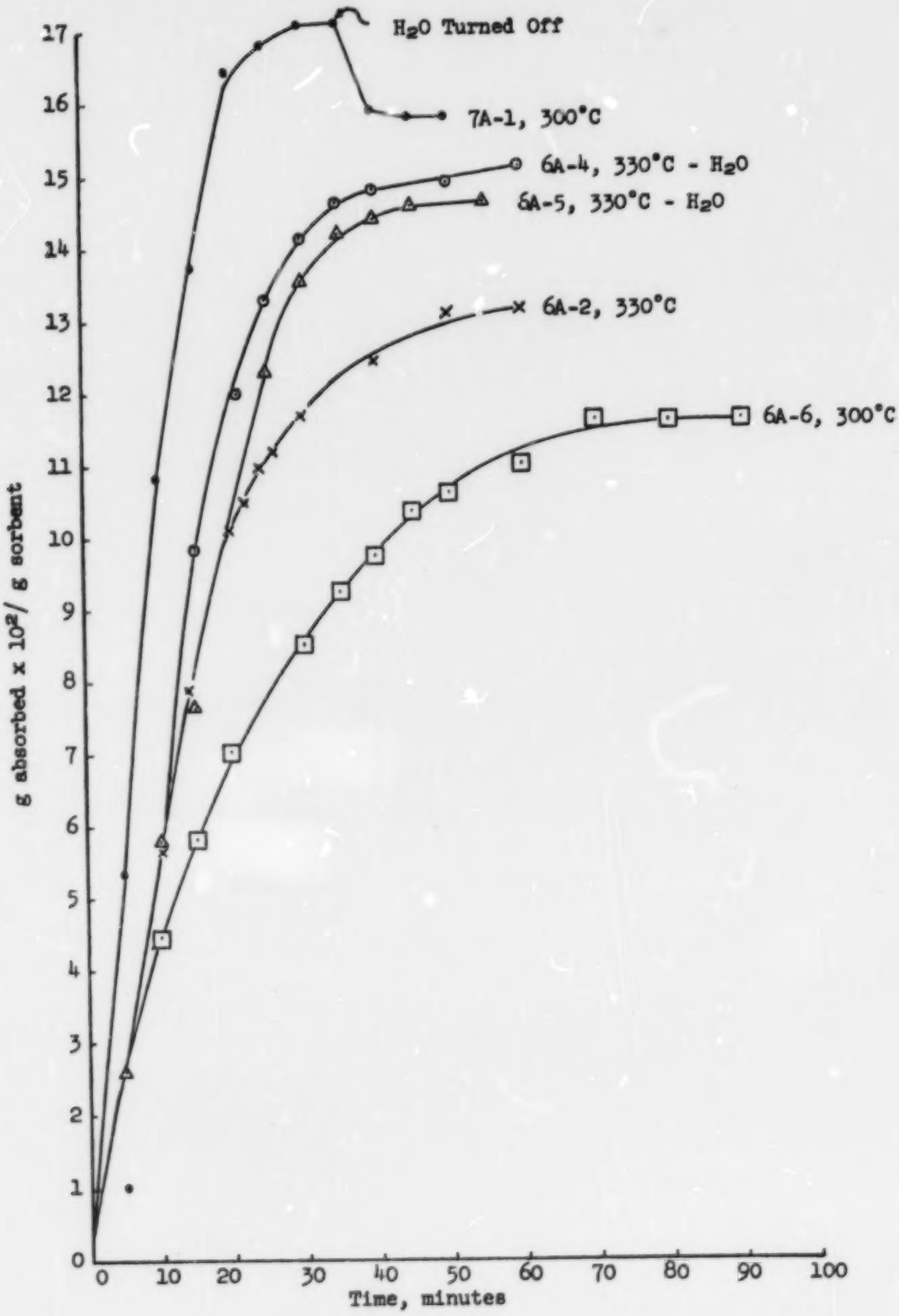
b. Effect of water vapor

The effect of water vapor as shown in the absorption curves plotted in Figure 6, is to increase the total weight of SO_3 absorbed with a slight increase in absorption rate. Part of the increased weight results from water being absorbed as sulfuric acid. In run 7A-1, the water flow

CCC 69-31

FIGURE 6

EFFECT OF H_2O VAPOR



CCC 69-31

was turned off, and the weight absorbed dropped sharply; however, the total weight absorbed remained greater than in run 6A-2 in which no water vapor was present.

c. Effect of nitrogen oxides

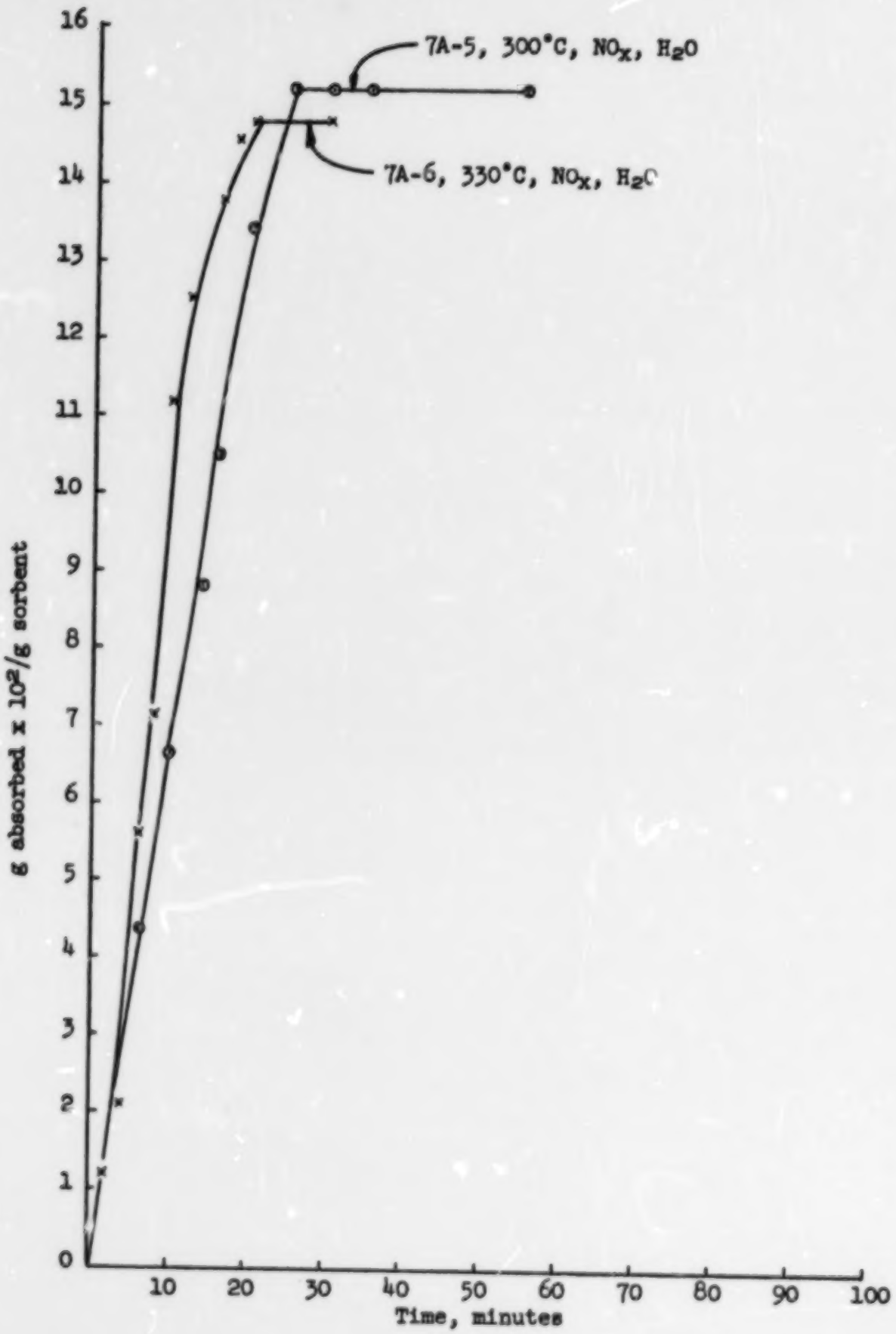
The introduction of nitrogen oxides did not markedly affect the SO_3 absorption rate. The results are shown in Figure 7, runs 7A-5 and 7A-6, and Table V. The absorption rate constant for run 7A-6 at 330°C is about the same as that obtained in the 6A series at this temperature.

A feed gas mixture containing SO_2 (3100 ppm), NO (500 ppm) and oxygen (approximately 2%) was passed through the catalytic converter and then mixed with H_2O vapor in the pre-heat zone. The stream to the absorber thus consisted of SO_3 (2300 ppm), SO_2 (800 ppm), NO and NO_2 (500 ppm combined) and H_2O about 7%.

CCC 69-31

FIGURE 7

EFFECT OF NO_x IN FLUE GAS



CCC 69-31

TABLE V

EXPERIMENTAL RESULTS

Run	6A-6	7A-5	7A-6
Temp., °C	300	300	330
Sorbent particle size, mesh	10-16	10-16	10-16
Sorbent weight, grams	0.4060	0.3913	0.3913
Weight % Na_2SO_4	25	25	25
Mmoles Na_2SO_4 on sorbent	0.715	0.689	0.689
Feed gas, SO_2 ppm	2050	3050	3050
Feed gas, NO_x ppm	0	500	500
Feed gas, H_2O %	0	7	7
Feed gas, O_2 %	2	2	2
SO_3 converter efficiency, before, %	73.3	67	108
SO_3 converter efficiency, after, %	74.0	87	63
SO_3 converter efficiency, average %	73.7	77	86
SO_3 pressure, inlet, atmos	.00151	.00235	.00262
Gas flow, cm^3/min.	930	1100	1100
SO_3 absorbed in 10 min., g/g sorb.	0.045	0.068	0.102
SO_3 absorbed in 10 min., grams	0.0183	0.0265	0.0399
SO_3 fed in 10 min., grams	0.0501	0.0925	0.1030
SO_3 absorbed, % of SO_3 in gas	36.5	28.7	38.8
SO_3 pressure, outlet, atmos	.00096	.00167	.00160
SO_3 pressure, average, atmos	.00124	.00201	.00211
SO_3 pressure, equilibrium, atmos	.00015	.00015	.00034
k, rate constant lbs SO_3/hr x lb sorb x (Y-Ye)	248	220	346

CCC 69-31

d. Effect of temperature

The effect of temperature is masked by the marked effect of equilibrium SO_3 pressure as illustrated by run 4A-3, Figure 8. This run was started at 375°C, which is close to the equilibrium temperature at the feed gas composition. The curve levelled off with a small amount of SO_3 absorbed. The temperature was then reduced to 325°C, and the absorption increased markedly to a rate comparable to other experiments carried out at 330°C.

The effect of temperature can be estimated by comparing calculated absorption rate constants as shown in the following table:

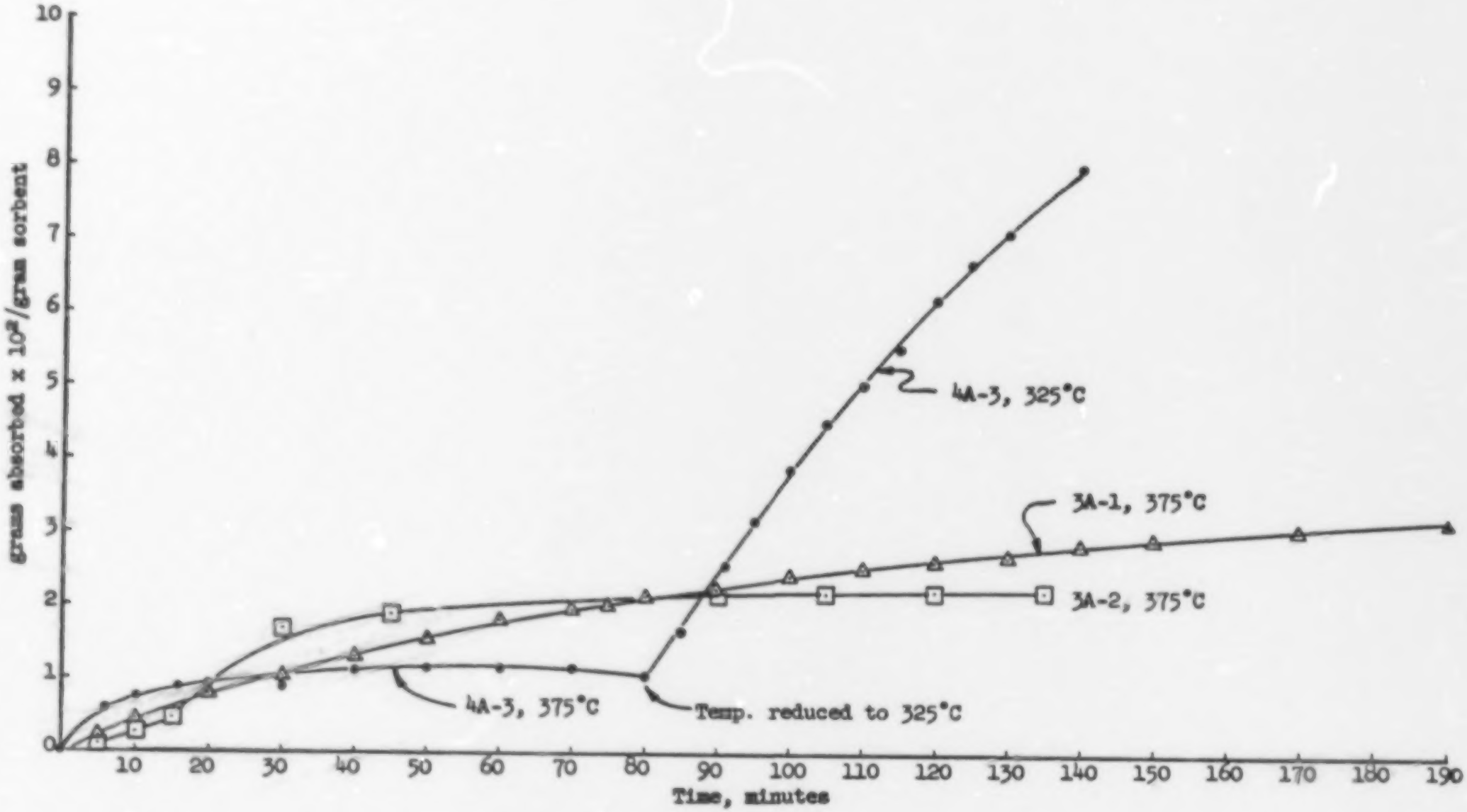
TABLE VI

EFFECT OF TEMPERATURE ON ABSORPTION RATE

	Absorption Rate	
Temperature	300°C	330°C
Run 6A-6	248	
7A-5	220	
7A-6		346
6A-2		372
2A-4	—	295
Average	234	338

FIGURE 8

EFFECT OF EQUILIBRIUM SO_3 PRESSURE



CCC 69-31

e. Effect of Na_2SO_4 conversion

Absorption curves shown in Figure 6 for the 6A and 7A series are essentially straight lines throughout the operating range (0 to 60% of sorbent capacity), and it was assumed for this evaluation that the absorption rate does not vary with the extent of conversion of Na_2SO_4 to $Na_2S_2O_7$. However, in studies carried out near equilibrium conditions, it is apparent that the equilibrium SO_3 pressure varies with the composition of the sorbent.

Runs 6E-4 and 6E-5, Figure 9, were carried out to study equilibrium conditions by increasing the temperature at the end of absorption runs while maintaining the same SO_3 flow. The SO_3 concentration was about 1700 ppm in both runs. At 375°C, equilibrium was reached at this SO_3 pressure when 30.6% of the Na_2SO_4 had been converted. The equilibrium conversion for run 6E-4 at 408°C was 19.2%. A similar effect was observed in run 5E-1, plotted in Figure 10.

Rate and equilibrium studies at low gas concentrations were carried out in runs 10-A-1, 2 and 3, Figure 11. Further data is needed to define the equilibrium SO_3 pressure over the Na_2SO_4-$Na_2S_2O_7$ solid solution. However, the effect of the solid solution is to reduce the SO_3 back pressure and facilitate absorption. It is also possible that the solid solution facilitates the transport of SO_3 within the particle. This may explain the lack of diffusional resistance encountered.

CCC 69-31

FIGURE 9

EQUILIBRIUM STUDIES
SO_3 pressure 0.0017 atmos.

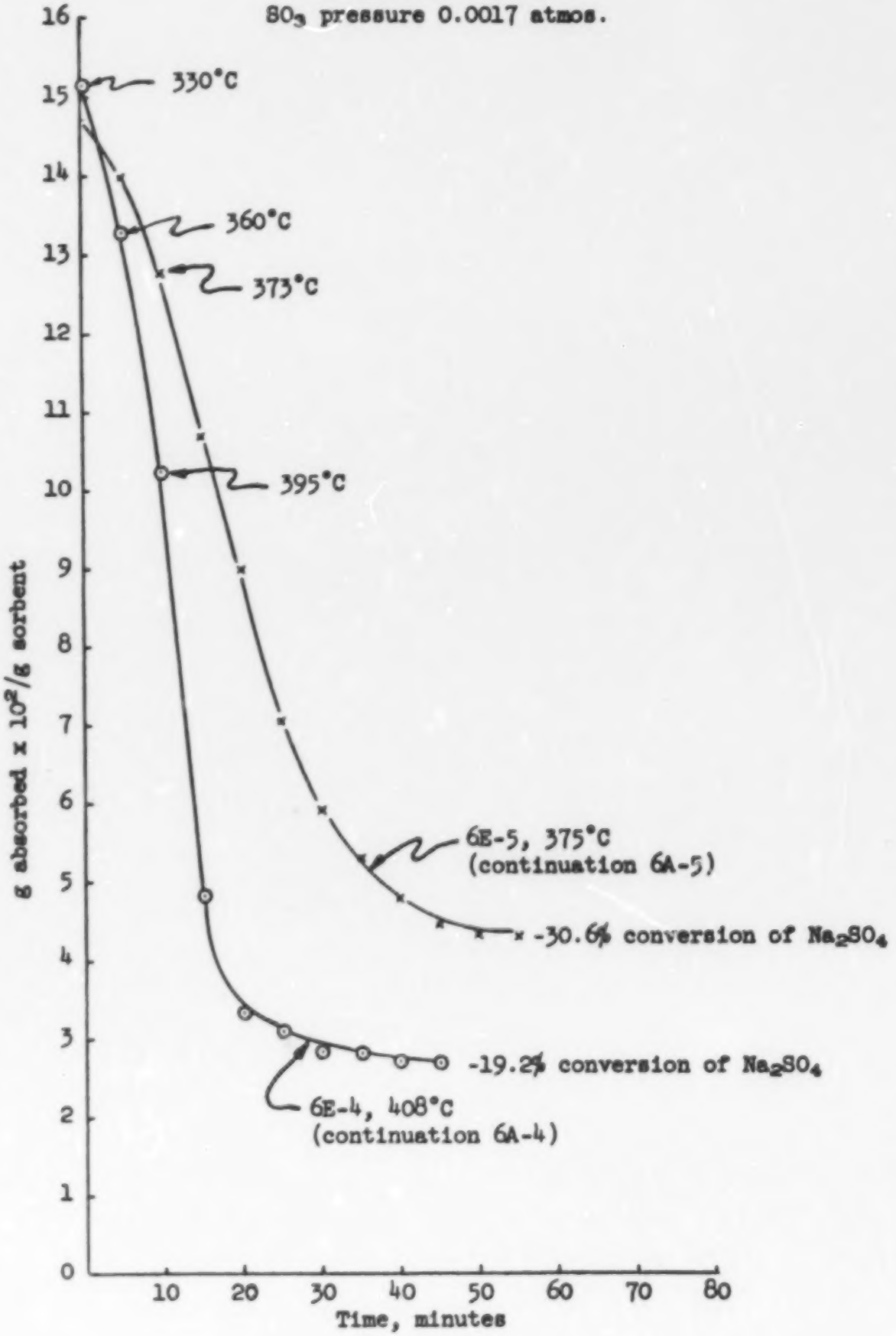


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FIGURE 10

EQUILIBRIUM STUDIES

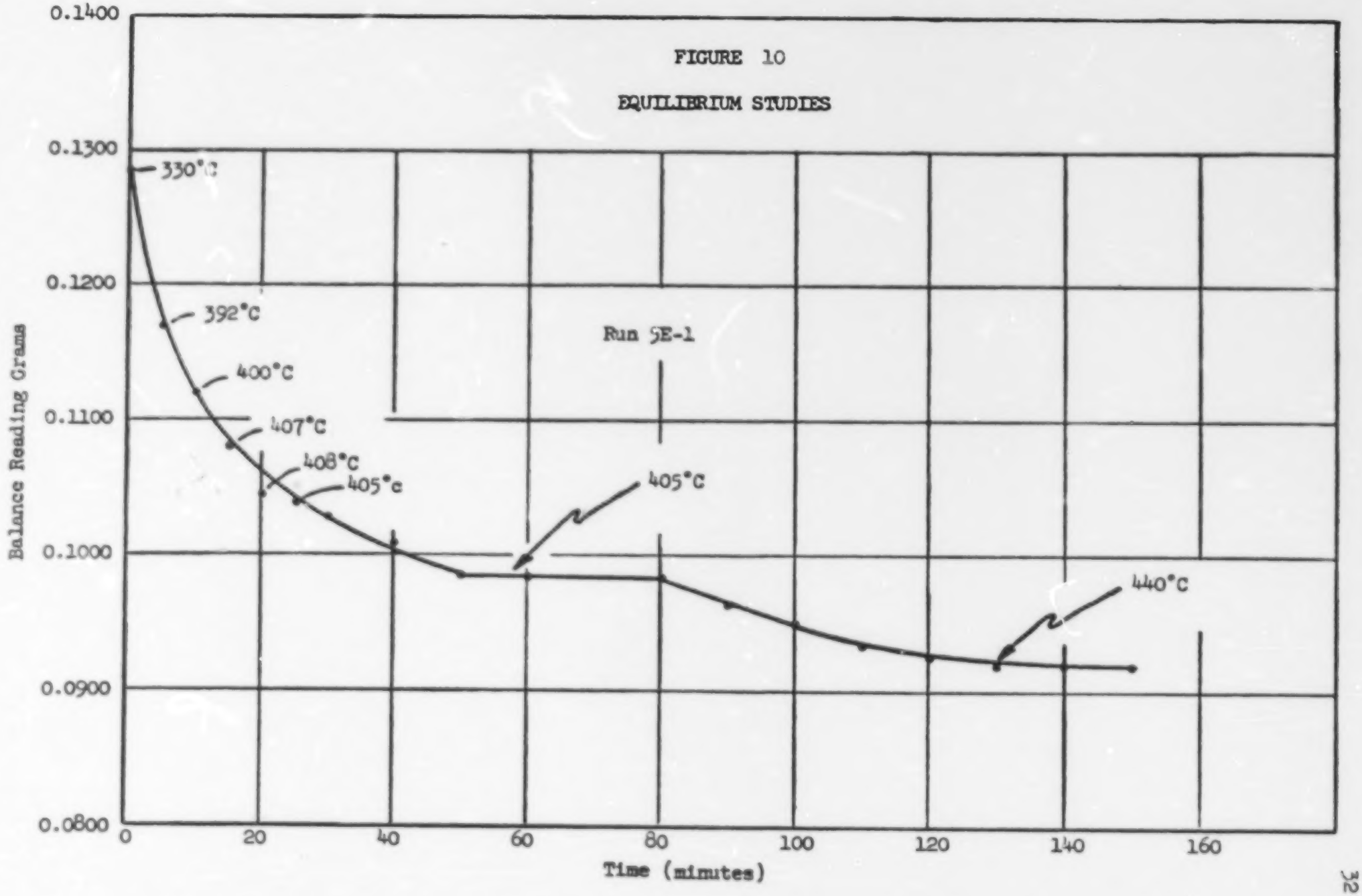

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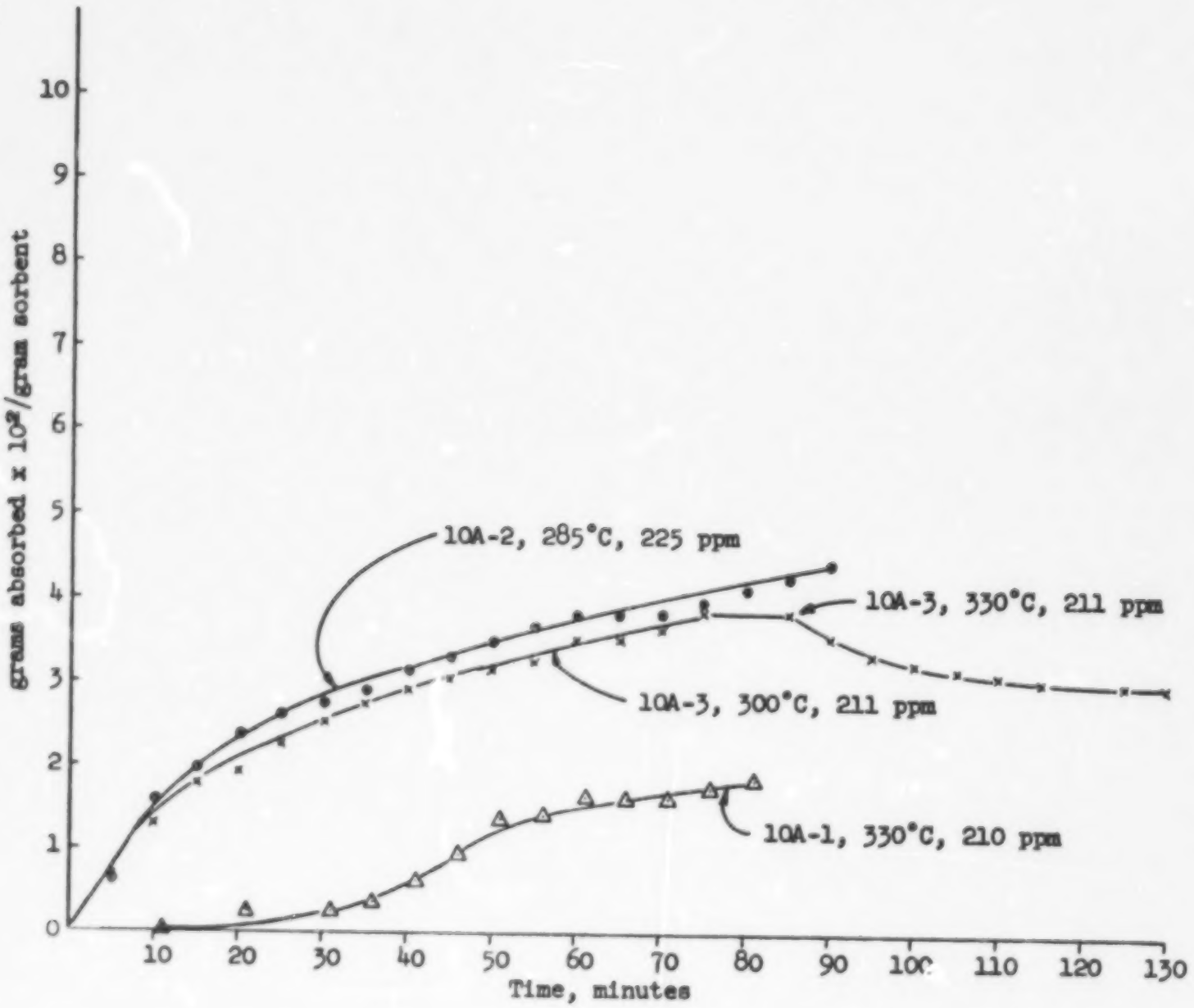
FIGURE 11

ABSORPTION STUDIES AT LOW SO_3 CONCENTRATION



CCC 69-31

f. Effect of fly ash substrate

A preliminary investigation was started on the use of fly ash substrate after the importance of sorbent cost was developed in economic studies. The limited experimental work on fly ash is quite encouraging, but was not carried far enough to fully demonstrate feasibility. Although fly ash has considerably less surface than silica gel, it is believed to be suitable for sorbent use because diffusion into the particle was not found to be a rate limiting step.

Fly ash was screened and samples treated with Na_2SO_4 solution in order to obtain a substrate suitable as a replacement for the silica-based material. Samples in the size ranges of 0.046 inches - 0.078 inches and 0.028 inches - 0.046 inches were treated overnight with a saturated solution of Na_2SO_4, the mixture filtered and the residue dried at 125°C. Sulfur analyses showed a 9.7 weight percent Na_2SO_4 content for the 0.046 - 0.078 inch (10-16 mesh) fraction and a 17.0 weight percent content for the smaller sized fraction. Retreatment of the 10-16 mesh fraction raised the Na_2SO_4 content to 19.9 weight percent.

A sample of fly ash-based absorbent was subjected to two cycles of SO_3 absorption and desorption. The sample contained 19.9 weight percent Na_2SO_4 absorbed on a screened sample of fly ash in the size range of 0.046-0.078 inches (10-16 mesh). The Na_2SO_4 loading was similar and the size range identical to the previously tested silica gel-based absorbent, allowing for a nearly direct comparison. The absorption was carried out

CCC 69-31

at 330°C, the desorption at 550°C. The results are shown graphically in Figures 12 and 13.

The slopes of the nearly constant rate of pick up for the fly ash substrate (Runs 8A-1 and 8A-2) are higher than those for the silica substrate (Runs 6A-1 and 6A-2) which are shown for comparison. The total weight gains in the comparison are misleading because the fly ash substrate is more dense, and thus the reactor holds more sample. Actually, the percent conversions of Na_2SO_4 to $Na_2S_2O_7$ for the silica substrate is significantly higher than for the fly ash substrate (Table 7).

TABLE VII

Na_2SO_4 CONVERSION ON SILICA AND FLY ASH

Run No.	Substrate	Na_2SO_4 Content (%)	Na_2SO_4 Content (mmoles)	SO_3 Absorbed (mmoles)	SO_3 Absorbed (% of Na_2SO_4)
6A-1	silica gel	25	0.715	0.608	85
6A-2	silica gel	25	0.715	0.666	93
8A-1	fly ash	20	1.605	0.993	62
8A-2	fly ash	20	1.605	0.856	53

The rapid and consistent take up of SO_3 right up to a sharp cut-off indicates that all of the available Na_2SO_4 was rapidly converted. The curves give no indication of a diffusion-limited absorption phase.

The desorption of SO_3 from the fly ash-based absorbent at 550°C was slow. Our previous experience with the silica-based absorbent under these conditions showed the SO_3 to be completely removed in a matter of minutes from the time the nitrogen sweep was initiated. In contrast,

CCC 69-31

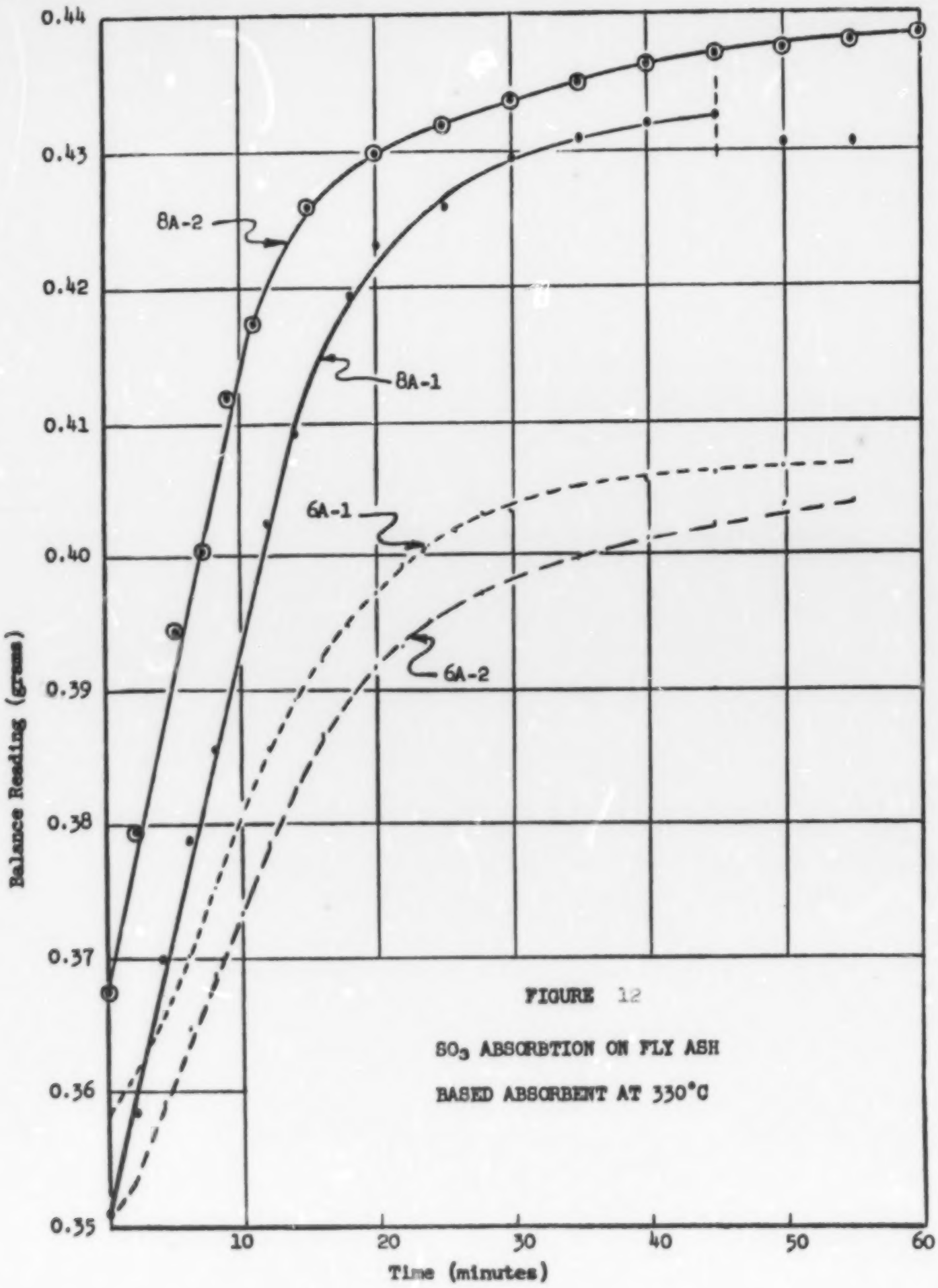


FIGURE 12

SO_3 ABSORBTION ON FLY ASH

BASED ABSORBENT AT 330°C

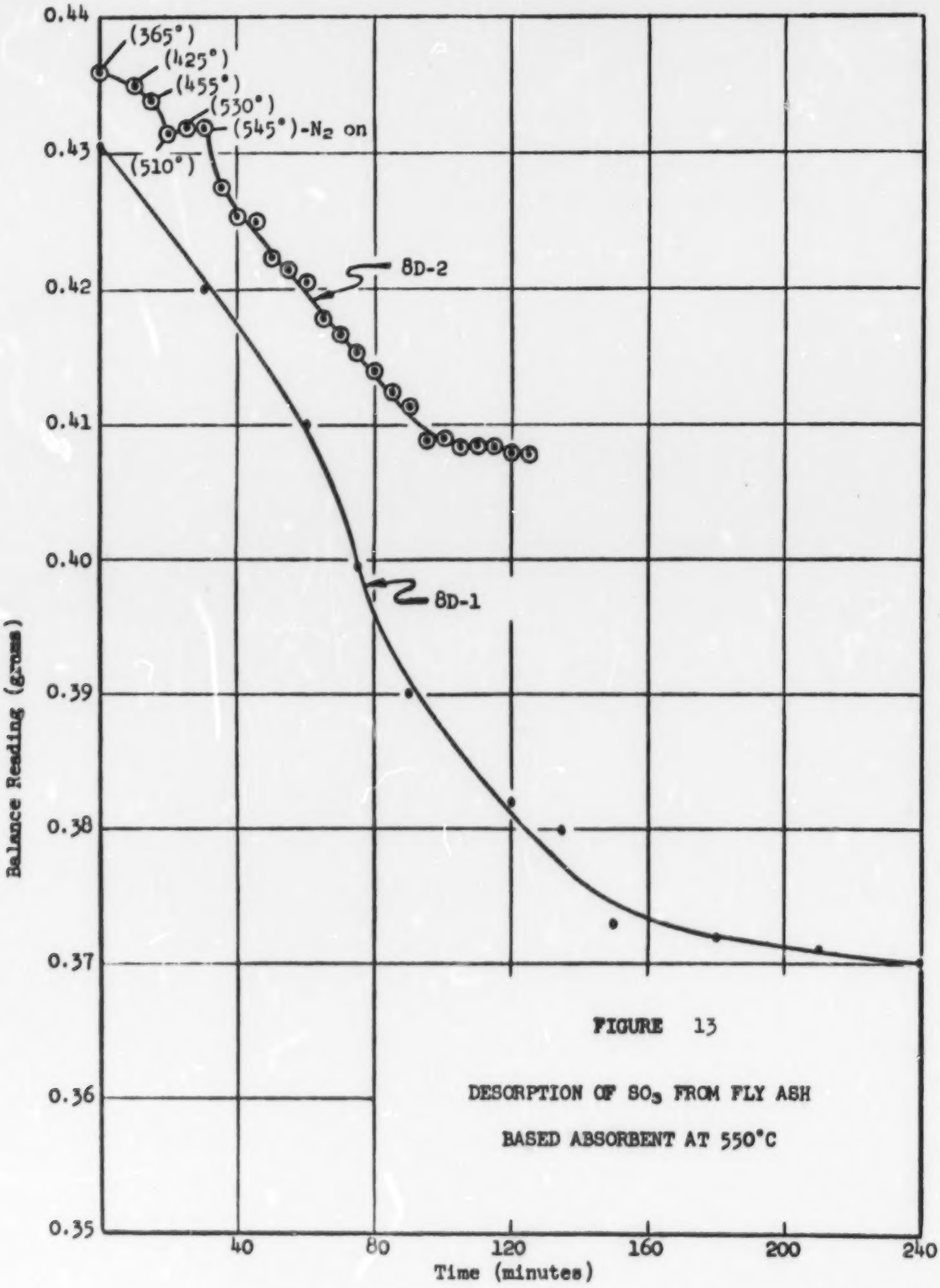


FIGURE 13

DESORPTION OF SO_3 FROM FLY ASH BASED ABSORBENT AT 550°C

CCC 69-31

the desorption of SO_3 from the loaded fly ash absorbent went only to the extent of 76% in run 8D-1 and only 41% in run 8D-2 in periods of two hours or more. The data are plotted in Figure 13.

We had expected that basic materials in fly ash would permanently hold up some SO_3, but that this effect would diminish after several cycles. This is still believed to be a valid assumption.

3. Desorption of SO_3

Desorption of SO_3 was found to be rapid and essentially quanitative. A nitrogen sweep at the rate of 200 cc/min was used to give a SO_3 concentration in the gas effluent of approximately 6%. At 500°C, about 88% of the absorbed SO_3 was released rapidly. The remainder came off very slowly at this temperature, but was released completely by raising the sample temperature to 550°C.

Typical desorption curves are shown in Figures 14 and 15. The SO_3 recovery data is summarized in Tables VIII and IX.

TABLE VIII

SO_3 RELEASE AT VARIOUS TEMPERATURES

Run No.	Release Temp. °C	Initial Rate SO_3 Release g/min.	mmoles/min.	SO_3 Conc. (mole %)
3D-3	500	0.020	0.25	2.7
2D-2	530	0.014	0.18	2.0
2D-3	540	0.043	0.54	6.0
4D-2	550	0.055	0.69	7.2

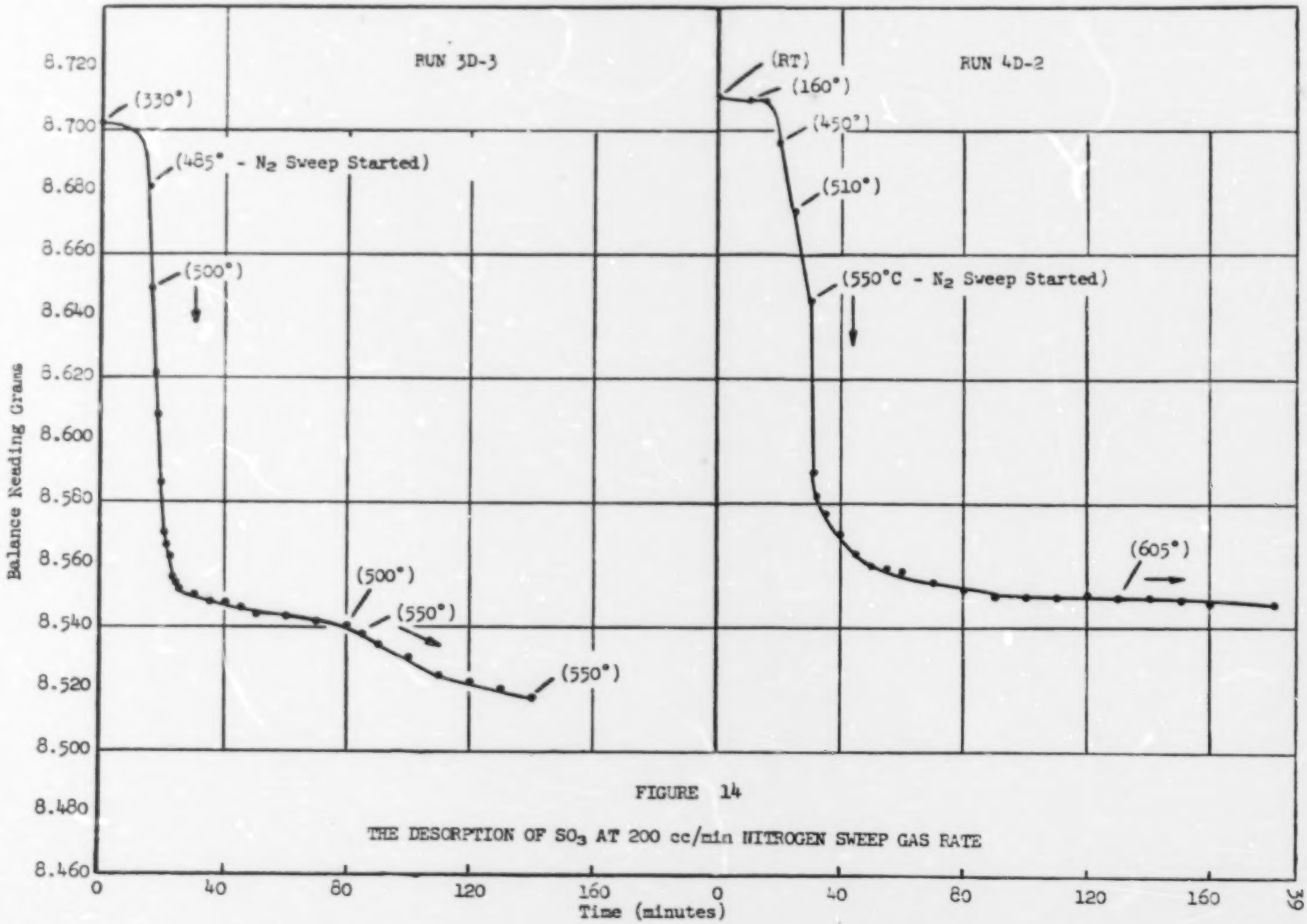


FIGURE 14

THE DESORPTION OF SO_3 AT 200 cc/min NITROGEN SWEEP GAS RATE

FIGURE 15

THE DESORPTION OF SO_3 AT 550°C AND 200 cm^3/min NITROGEN SWEEP GAS RATE

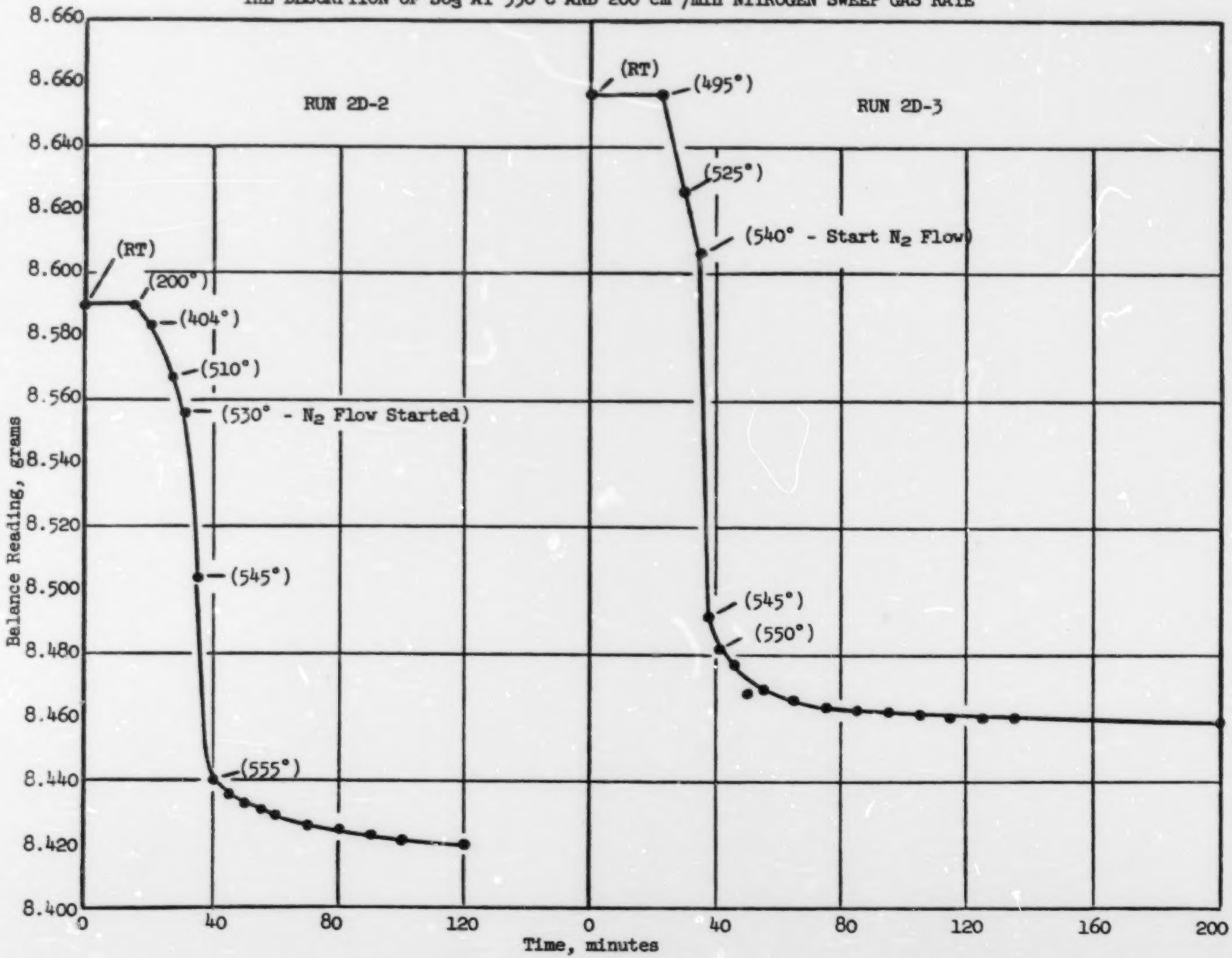


TABLE IX

MATERIAL BALANCE, SO_3 ABSORPTION AND DESORPTION

Run No.	SO_3 Absorbed (mmoles)	SO_3 Desorbed (mmoles)	SO_3 Desorbed (% Recovered)
2D-1	1.781	1.638	92
2D-2	2.044	2.124	104
2D-3	2.595	2.485	96
3D-1	0.844	0.794	94
3D-3	2.545	2.320	91
4D-2	1.918	2.038	106
4A-3	1.873	1.794	96
6A-2	0.666	0.635	95
6A-3(with H_2O)	0.741	0.769	104
6A-4(with H_2O)	0.769	0.781	102

4. Fly Ash Catalyst

The catalyst composition required for conversion of SO_2 to SO_3 is essentially the same as the sorbent composition with the addition of V_2O_5. Since considerable carry over of catalyst into the sorbent is anticipated, it would be advantageous to make the materials identical and use a single catalyst-sorbent. Although catalyst investigation is not within the scope of this program, a preliminary experiment was carried out to show the feasibility of this concept.

A portion of the 10-16 mesh fly ash was treated with K_2SO_4 and V_2O_5 in water and the mixture evaporated to dryness at 120°C over a five hour period. The mixture consisted of the following:

Reagent	Weight (g)	Weight %
fly ash	50	85
K_2SO_4	5.8	10
V_2O_5	3.0	5

CCC 69-31

The total charge of 33.8 g was placed in the converter tube and heated to 200°C for two hours while passing a slow flow of nitrogen for further drying. SO_2 (3050 ppm), NO_x (500 ppm) and O_2 (ca. 2%) were then started through the converter at 450°C at a total flow of about 900 cc/min to condition the catalyst. No misting, indicative of SO_3 formation, was noticeable in the trap section after 6 hours. However, after running overnight (21 hours total) the SO_3 production was considerable. Converter efficiencies were then tested periodically with the following results:

Calibration Run No.	Hrs. From Initiation	Conversion %
1	23	68
2	25	134
3	30	118
4	32	77
5	35	87
6	37	87

Pressure fluctuations because of faulty valve action probably resulted in our high result in Run 2. Fly ash residue was swept into the valve seat. This may have carried over into calibration Run 3. According to published reports(2), SO_3 catalysts are slow to come to equilibrium, and at low concentrations, this problem may be magnified. At any rate, the last three runs were promising, being comparable to the results obtained under our operating conditions with the commercial Harshaw catalyst.

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(2) H. F. A. Topsoe and A. Nielsen, "The Action of Vanadium Catalyst in the Sulfur Trioxide Synthesis".

CCC 69-31

III. ECONOMIC EVALUATION

A Description of Process

1. Sulfuric Acid Production

The process flow sheet and operating conditions for removal of SO_2 from flue gas and conversion to sulfuric acid are shown on Figure 16. The process is based on the reversible reaction of SO_3 with sodium sulfate to form sodium pyrosulfate according to the following reaction:

$$Na_2SO_4 + SO_3 \rightleftarrows Na_2S_2O_7 .$$

SO_2 in the flue gas is first oxidized to SO_3, and the SO_3 is absorbed from the gas by reaction with Na_2SO_4 impregnated on a fly ash substrate. The fly ash substrate is impregnated with about 25 weight percent Na_2SO_4 and 5 weight percent of V_2O_5 in order that the same material may be used for oxidation catalyst and sorbent.

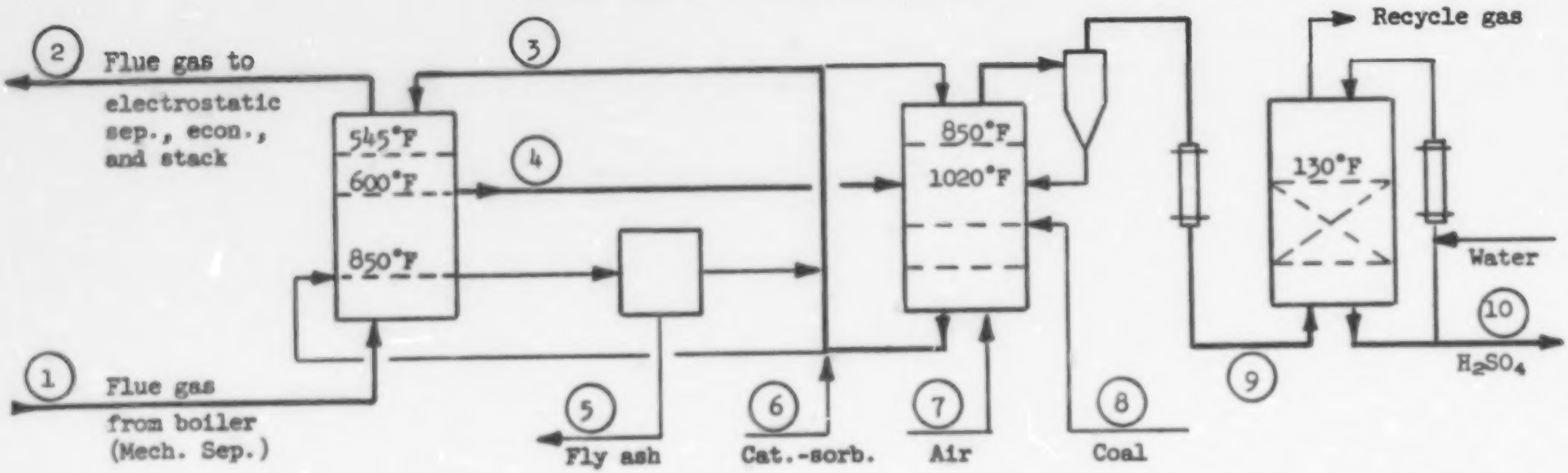
The catalyst-sorbent is continuously circulated through the fluid bed oxidation zone to an air separator where fly ash from the boiler is removed. Ninety percent conversion of SO_2 to SO_3 has been assumed.

After passing through the oxidation zone, flue gas is cooled from 850°F to 545°F by heat exchange with boiler air and passed through two fluid absorption beds designed for removal of 95% of the SO_3. Flue gas is drawn from the converter-absorber at about 8 inch water vacuum by an exhaust fan, and passed to an electrostatic precipator, economizer and stack, all of which are considered to be part of the power plant.

FIGURE 16

FLOW SHEET - H_2SO_4 PRODUCTION

1400 MW Boiler, 0.2% SO_2 in Flue Gas



	Converter-absorber 85 ft x 130 ft x 160 ft high	Air Separator	Desorber 41 ftØ x 40 ft	SO_3 Absorber 30 ft Ø x 30 ft

Stream	1	2	3	4	5	6	7	8	9	10
Temp., °F	850	545	545	600	800	100	100	100	450	230
Pressure, psia	14.7	(8"H_2Ovac)	14.7	14.7	14.7	14.7	16.4	16.4	15	14.7
SO_2 M lbs/hr	51	5.1								
SO_3 "		2.8		54					54	
N_2 "	8286	8286.0					230		230	
CO_2 "	2555	2555.0							30	
H_2O "	516	511.0		5			3		8	
O_2 "	354	342.6					66		44	
Cat.-sorb. "		0.8	614	614		0.8				
Fly ash "	10				10					
H_2SO_4 "										66
Coal "								8.2		
Total "	11,772	11,703.3	614	673	10	0.8	299	8.2	366	66

CCC 69-31

Sorbent, rich in SO_3, is air conveyed to the desorber where SO_3 is released at a temperature of 1020°F and at a concentration of about 6% in an air stream heated by direct injection of powdered coal. The sorbent is held in the fluid desorption bed for 20 minutes to insure complete removal of SO_3, and then passed down through two fluid beds where it is cooled to 545°F by contact with the desorption air stream.

At 1020°F the SO_3 will disproportionate partially to $SO_2 + O_2$; therefore, the SO_3 gas is cooled to 850°F and passed through a catalyst-sorbent fluid bed to convert this SO_2 back to SO_3.

The SO_3 gas stream from the desorber is cooled to 450°F and passed through the SO_3 absorber where SO_3 is absorbed in a circulating stream of concentrated sulfuric acid. Off gas containing any SO_2 or SO_3 not absorbed is recycled back to the converter-absorber.

2. Concentration of SO_2

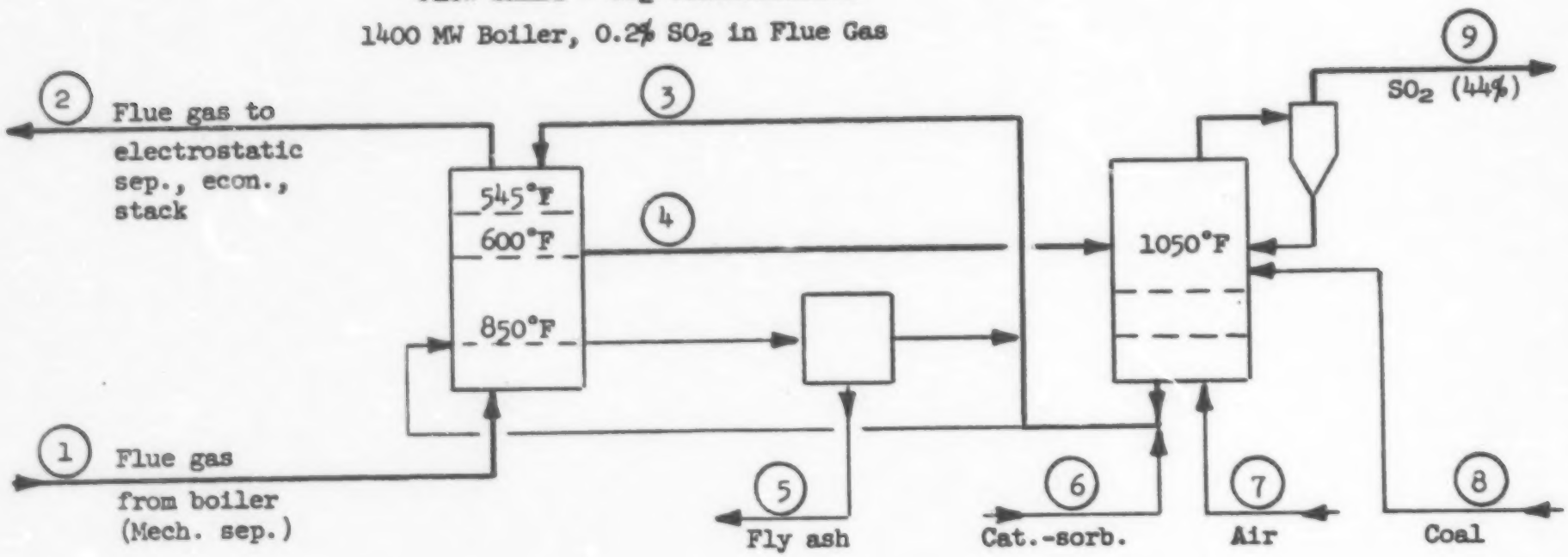
The possibility of using this process as a means of concentrating SO_2 for subsequent reduction to sulfur was considered as a result of the concern expressed by men in the power plant field over disposal of sulfuric acid. The flow sheet and operating conditions for concentrating the SO_2 to about 44% (by volume) are shown on Figure 17.

Production of concentrated SO_2 is accomplished by limiting the air flow to the desorber, thus driving the disproportionation reaction, $SO_3 \longrightarrow SO_2 + 1/2\ O_2$, to completion by removal of the oxygen to form CO_2.

FIGURE 17

FLOW SHEET - SO_2 CONCENTRATION

1400 MW Boiler, 0.2% SO_2 in Flue Gas



Converter-absorber
85 ft x 130 ft x 160 ft high

Air Separator

Desorber
18 ft ø x 70 ft

Stream		1	2	3	4	5	6	7	8	9
Temp., °F		850	545	545	600	800	100	100	100	1050
Pressure, psia		14.7	(8"H_2O-vac)	14.7	14.7	14.7	14.7	20.7	20.7	14.7
SO_2	M lbs/hr	51	5.1							43.2
SO_3	"		2.8		54					
N_2	"	8286	8286.0					5.3		5.4
CO_2	"	2555	2555.0							17.0
H_2O	"	516	511.0		5			0.1		5.1
O_2	"	354	342.6					1.5		
Cat.-sorb.	"		0.8	614	614		0.8			
Fly ash	"	10				10				
Coal									4.6	
Total		11,772	11,703.3	614	673	10	0.8	6.9	4.6	70.7

CCC 69-31

The dissociation pressure of $Na_2S_2O_7$ reaches one atmosphere at about 1242°F. If all of the oxygen were removed by carbon to form CO_2, it should be possible to produce a gas mixture containing 2/3 SO_2 and 1/3 CO_2. Under the design conditions shown in Figure 17, the SO_2 concentration is limited to about 44% by water picked up by the sorbent and by the air flow needed for fluidization and heating.

B. Special Features

The particular advantages offered by this process are summarized as follows:

1. The reaction is rapid, reversible, and clean; that is, there are no problems with side reactions or by-products other than sulfuric acid.
2. The sharp change of SO_3 partial pressure with temperature permits a cyclic process to operate over a narrow temperature range.
3. Sulfur in flue gas can be converted either to concentrated sulfuric acid or a concentrated SO_2 stream suitable for reduction to sulfur.
4. Reducing agents are not required when producing sulfuric acid.
5. Sorbent can be regenerated at relatively low temperature.
6. Catalyst-sorbent is inexpensive and expendable. (The V_2O_5, which represents most of the sorbent cost, could be recovered partially from the electrostatic precipitator. This recovery was not considered in the present cost analysis.)
7. A novel, low pressure, fluid contactor has been suggested. This

design is believed to offer advantages for the high volume, low pressure flue gas application.

8. Corrosion problems are minimized.

C. Cost Summary

We can visualize problems in disposing of sulfuric acid at many, perhaps the majority of power plant locations. However, the special case in which a large new power plant is located near or adjacent to a sulfuric acid consuming industry is believed to warrant consideration because this may be the only case in which an economically attractive recovery situation can be developed. The present trend of locating the power plant at the mine could lead to such a situation.

Following is a summary of estimated capital and operating costs:

1400 MW Power Plant, 0.2% SO_2 in Flue Gas
Operating 330 days/year at 70% Capacity

		Concentration of SO_2 to 44%	Sulfuric Acid Production
Capital investment		$ 7,880,000	$ 10,220,000
	$/KW	5.63	7.3
Operating cost	$/year	2,590,000	3,250,000
	$/ton coal	0.81	1.01
	mil/kwh	0.33	0.42
Break even acid price			
	$/ton H_2SO_4	---	17.80

D. Catalyst-sorbent

Most processes for recovery of SO_2 from flue gas will require a carrier for transport of the sulfur. Carrier losses, which

CCC 69-31

necessarily result from the high gas volume and fly ash contamination, represent a major operating cost factor. The approach we have taken is to accept considerable loss, emphasizing a low cost granular carrier.

It is apparent that the silica gel substrate employed during the bulk of our experimental program is better than necessary, since no internal diffusional resistance was observed within the cperational range of saturation. In seeking a silica-alumina substrate which would be compatible with flue gas at elevated temperature and be available in large volume at low cost, the advantages of fly ash became obvious.

Experimental work using fly ash was limited to preliminary experiments (described in the experimental section of this report), and conditions for making suitable catalyst-sorbent were not determined. However, an indication of feasibility was obtained for using fly ash substrate both as a catalyst and as a sorbent.

The surface area of the fly ash granules is considerably less than that of silica gel. However, we visualize making a material with adequate surface by incorporating a basic material such as soda ash or lime in the impregnating solution. The basic material will react with fly ash to form a cement like structure. We visualize carrying this impregnating reaction out in a ball mill to give the desired particle size.

Assuming that this relatively simple processing operation will yield a suitable catalyst-sorbent, the material and capital costs were

calculated as follows:

Sorbent make up (0.1% of feed)		
614,000 lbs/hr x 0.001 x 7920 hrs/yr	=	4,850,000 lbs/yr
Catalyst make up (1% of inventory/day)		
20,000 ft^3 x 25 lbs/ft^3 x 0.01 x 330 days/yr	=	1,650,000 lbs/yr
Total make up		6,500,000 lbs/yr

Material Cost		
Na_2SO_4: 6.5 x 10^6 x 0.25 x \$0.017/lb	=	\$ 27,600/yr
V_2O_5 : 6.5 x 10^6 x 0.05 x \$1.40/lb	=	450,000
Total		\$ 477,600/yr
\$478,000/6.5 x 10^6 lbs	=	\$ 0.0735/lb catalyst-sorbent

Capital Cost - Processing Equipment
Est. Cost = \$280,000, Installed in place.

Labor Cost: One operator per shift was included in process operating cost estimate for catalyst-sorbent preparation.

It is recognized that the principal uncertainties in the recovery process are associated with the catalyst-sorbent. These uncertainties could, for the most part, be resolved through a relatively small experimental program, which has been proposed.

E. Converter-Absorber

1. Description of Contactor

A fluid bed gas-solid contactor is recommended for the converter-absorber. Fluid-bed processing is particularly well adapted to a large scale, single line type plant. We believe that a single line plant is much preferable to one having multiple lines of equipment in parallel, and that savings in piping, labor, etc., will be greater than are reflected in a factored cost estimate.

CCC 69-31

A somewhat novel type of low pressure contactor is proposed as shown in Figure 18. The contactor is essentially a normal, steel frame building with beds supported on internal columns. Approximate outside dimensions are 85 ft x 130 ft x 160 ft high. The building operates under a vacuum of about 8 inches H_2O created by the flue gas exhauster.

The contactor consists of four sections arranged vertically and operating in parallel. Flue gas, flowing at a velocity of 2.5 ft/sec., passes through three fluid catalyst-sorbent beds in series. The lower bed is seven inches deep and operates at 850°F to catalyze the oxidation of SO_2 to SO_3. The next two beds, having a total fluidized depth of 7-1/2 inches, operate at 625°F and 545°F respectively and provide for absorption of 95% of the SO_3 from the flue gas. The fluid beds are supported on 8 inch pipes which carry air to the boiler, thus providing for temperature control and mechanical tray support.

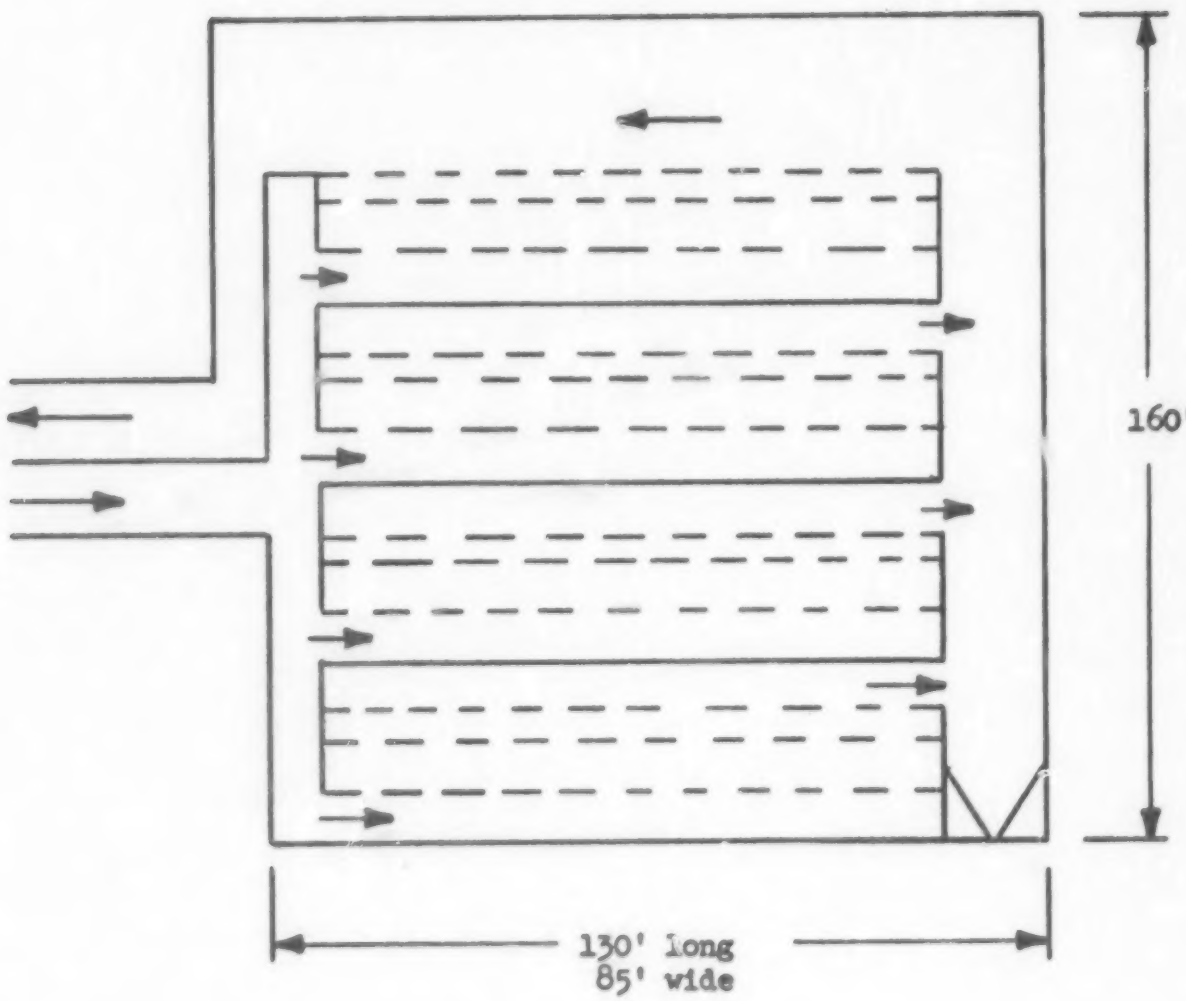
In the design proposed the duct work becomes part of the building. The flow pattern is difficult to analyze, but it is assumed that sufficient settling of solids from the gas phase occurs in the relatively low velocity horizontal and vertical ducts to eliminate the need for a cyclone separator ahead of the final electrostatic separator (assumed part of the power plant).

The principal advantage of this type contactor is low pressure drop. The cost installed in place is estimated to be $2,000,000 as compared to $2,500,000 for a conventional unit including cyclone separator. It is believed that the low pressure, low velocity type contactor warrants further

CCC 69-31

FIGURE 18

CONVERTER-ABSORBER



study; however, for the purpose of initial evaluation of process economics, the use of a more conventional type contactor and cyclone separator would not markedly affect the results.

2. Depth of Sorbent Required

The depth of catalyst-sorbent required for removal of 95% of the SO_3 in the flue gas was calculated based on the experimentally determined rate constant, and assuming that the rate is proportional to the SO_3 concentration in the gas minus the equilibrium SO_3 partial pressure, (Y-Ye).

The equilibrium SO_3 pressure was calculated based on free energy data as follows:

	$Na_2S_2O_7$	⟶	Na_2SO_4 +	SO_3	
ΔF_f	-410,400		-302,730	-88,545,	ΔF 298°K = + 19,125 cal.
ΔH_f	-455,600		-333,500	-94,450,	ΔH 298°K = + 27,650
C_p	51.2		33.8	17 ,	ΔC_p = - 0.4

K = Equilibrium constant = Partial pressure SO_3, atmos.

$\log K = -\Delta F/4.575\ T$

K, 298°K = 0.935×14^{-14} atmos.

Since ΔC_p is small, ΔH was assumed to be constant, and K calculated as a function of temperature by the following equation:

$$\log\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{4.575}\left(\frac{T_2 - T_1}{T_2 T_1}\right)$$

The solid line in Figure 19 shows the calculated equilibrium partial pressure of SO_3. The dashed line, which follows points determined

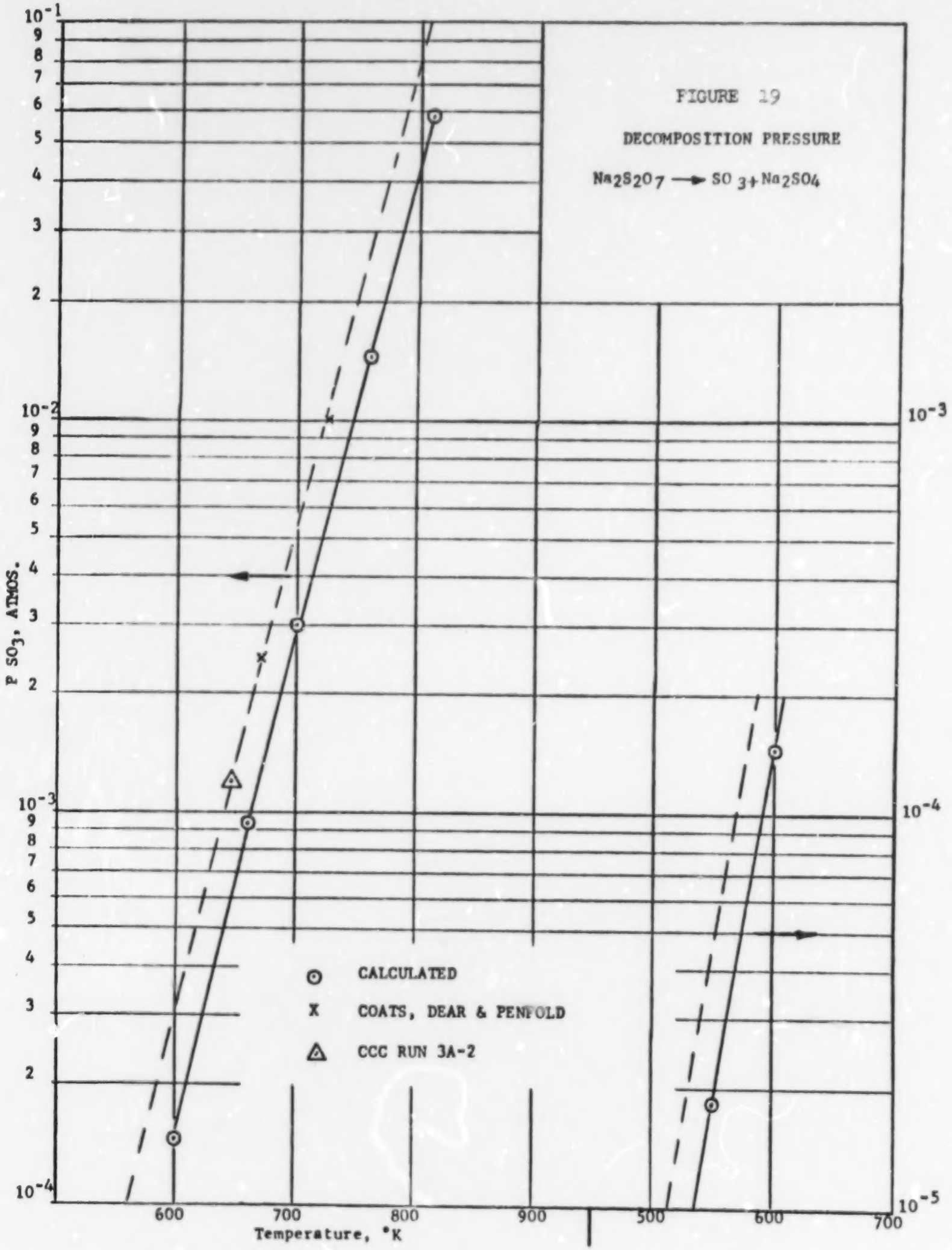


FIGURE 19
DECOMPOSITION PRESSURE
$Na_2S_2O_7 \longrightarrow SO_3 + Na_2SO_4$
P SO_3, ATMOS.
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
CALCULATED
COATS, DEAR & PENFOLD
CCC RUN 3A-2
600
700
800
900
500
600
700
Temperature, °K

experimentally by Coats et al[3] and by Callery indicates that the equilibrium pressure is somewhat higher than that calculated. Callery data also indicates that a solid solution is formed. Thus, the actual equilibrium pressure also depends on the extent of conversion of Na_2SO_4 to $Na_2S_2O_7$.

The absorption rate was found to be constant at 0.335 lbs SO_3/hr x lb sorbent up to about 67% of sorbent capacity or 0.088 lbs SO_3/lb sorbent. Thus, the sorbent circulation rate required is 614,000 lbs sorbent per hour (54,000 lbs SO_3/hr x 0.088). The depth of sorbent required was calculated assuming that the absorption rate is a function of (Y-Ye) according to the following equation:

$$G\ dY\ (M_{SO3}/M_G) = k\ \rho_{sf}\ (Y-Ye)\ d\ h$$

$$\frac{dY}{Y-Ye} = \frac{M_G\ k\ \rho_{sf}\ h}{M_{SO3}\ G}$$

G = Gas mass flow rate, lbs/hr ft^2
M_{SO3}, M_G = molecular weights of SO_3 and flue gas
k = absorption rate, lbs SO_3/hr x lb sorb x (Y-Ye)
ρ_{sf} = fluidized density of sorbent, lbs/ft^3
h = bed depth, ft.

The left hand side of the equation was integrated graphically between the limits of Y = 0.002 and Y = 0.0001 for 95% absorption of SO_3 to give a value of 5.07. Substituting an average reaction rate from experimental data, k = 310, and fluidized density, ρ_{sf} = 25 yields,

$$h = 0.00176\ G.$$

---

(3) Coats, A. W., Dear, D J.A. and Penfold, D
Phase Studies on the Systems, Na_2SO_4-SO_3, K_2SO_4-SO_3 and Na_2SO_4-K_2SO_4-SO_3
Journal of the Institute of Fuel, March, 1968, p 129.

At a superficial velocity of 2.5 ft/sec, the required bed area is 34,000 ft^2 and G = 346. At this mass velocity the required bed depth is 0.608 ft = 7.3 inches. Two beds having a total depth of 7.5 inches were selected.

F. Desorber

1. Sulfuric Acid Production

A sketch of the SO_3 desorption vessel required when operating to produce sulfuric acid is shown in Figure 20. The vessel is approximately 41 ft diameter by 40 ft high, and was assumed to be constructed of low alloy, Alonized steel. A cyclone separator is provided for removal of catalyst sorbent carried overhead.

Desorption of SO_3 from the sorbent has been shown to be very rapid at 1020°F, and is accomplished in a fluid bed 6 ft deep, sized to allow a sorbent residence time of 20 minutes. SO_3 is removed at a concentration of 6% in air heated by direct injection of powdered coal. After SO_3 removal, the sorbent passes down through two fluid beds where it is cooled to 545°F by the incoming desorption air stream.

At 1020°F SO_3 is partially dissociated. The extent of dissociation depends on the equilibrium constant and on the oxygen concentration as shown in the following equation:

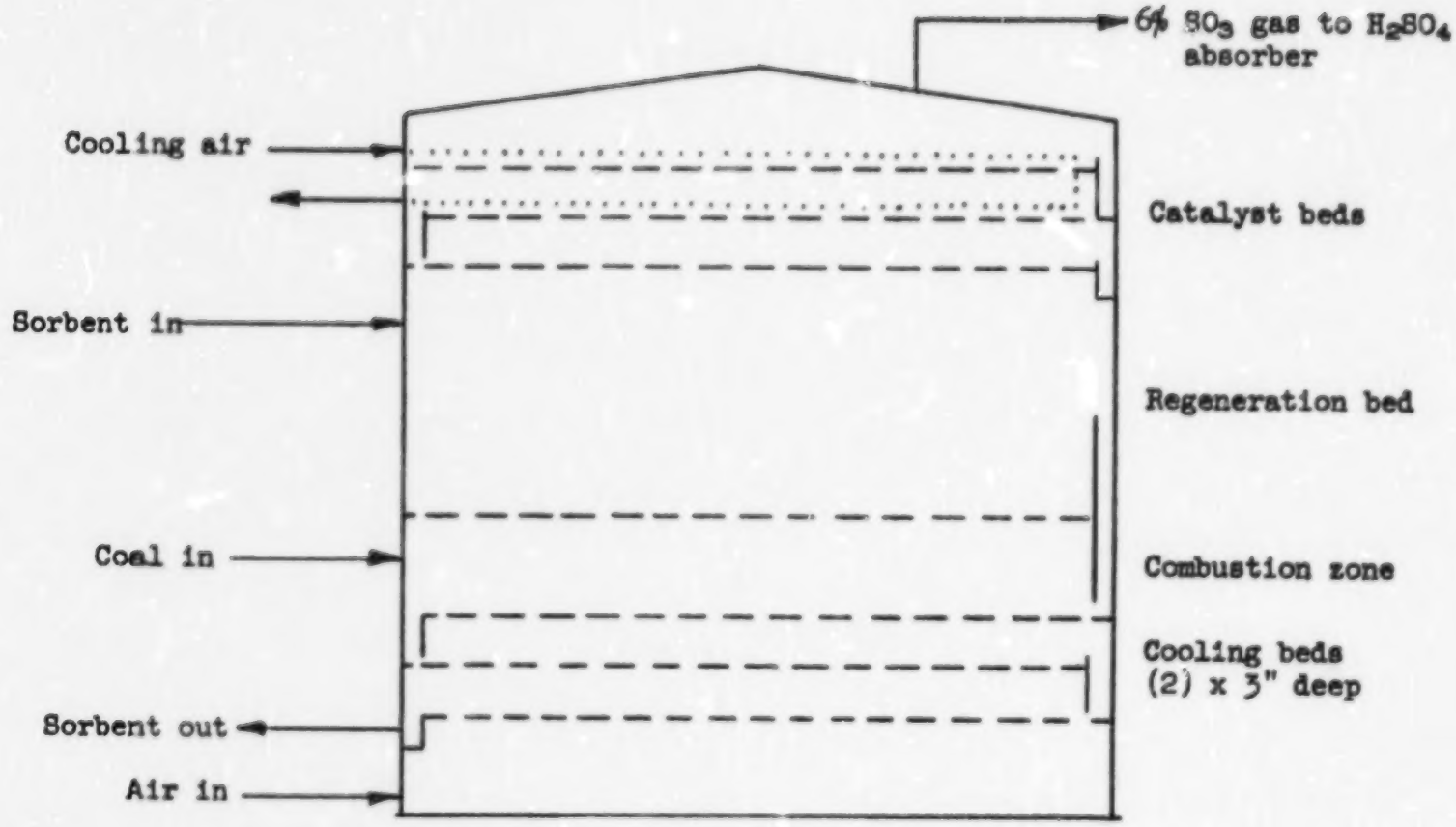
$$[SO_2] / [SO_3] = K/[O_2]^{\frac{1}{2}}$$

At the design conditions for sulfuric acid production the oxygen partial pressure is about 0.1 atmosphere and the equilibrium constant is 0.0437 at 1020°F. Inserting these figures, the $[SO_2]/[SO_3]$ ratio = 0.138, which indicates about 12% dissociation.

CCC 69-31

FIGURE 20

SO_3 DESORBER



41' diam. x 40' high

In order to convert the SO_2 back to SO_3 the gas stream is cooled to 850°F and passed through a catalyst-sorbent bed formed by recycling part of the stripped catalyst-sorbent back to the top of the desorber.

The possibility of sorbent particles sticking together has been considered, since liquid $Na_2S_2O_7$ could exist at temperatures above 750°F in the presence of a high concentration of SO_3. The minimum eutectic melting point in the Na_2SO_4-$Na_2S_2O_7$ system is 750°F at an SO_3 concentration of 2700 ppm. Thus, a liquid phase cannot exist in the converter-absorber unit, but could exist while the sorbent is being heated to 1020°F. Slight evidence of sticking was observed on removing the sorbent after multiple runs in the laboratory. However, under conditions used in the laboratory, the sorbent was heated to regeneration temperature before starting the nitrogen sweep. During the appreciable time period required for heating, conditions conducive to the formation of liquid $Na_2S_2O_7$ would exist. In the proposed plant design we expect to by-pass this problem by injecting the rich sorbent into the hot vapor space above the regeneration bed, where the sorbent surface should remain dry as a result of rapid evolution of SO_3.

The SO_3 concentration from the desorber was initially set at 6% in line with sulfur burning acid plant design. However, in this process, it is probable that a more economical design could be developed by going to a slightly higher temperature and higher concentration. Thus, the vessel size and power required for sorbent regeneration and SO_3 absorption in H_2SO_4 could be markedly reduced as a result of the smaller gas volume.

CCC 69-31

2. Concentration of SO_2

Operation of the desorber using a limited amount of air to produce a concentrated stream of SO_2 has not been tried experimentally. There would seem to be little doubt that it is possible to promote the disproportionation of SO_3 to SO_2 using carbon to maintain a low oxygen concentration. A temperature of 1050°F has been assumed for this evaluation, but a somewhat higher temperature may be desirable for increased reaction rate.

The drastically reduced air flow rate results in a much smaller desorption tower, blower and cyclone separator than are required for the conditions assumed for acid production. The desorber is 18 ft diameter by 70 ft high.

G. SO_3 Absorber

The SO_3 absorber is an acid proof brick lined tower 30 ft diameter by 30 ft high containing a 15 ft packed section. SO_3 is absorbed in sulfuric acid which is circulated over the packing and through an external cooler at the rate of 620 GPM.

The gas containing SO_3 enters the bottom of the absorber at 450°F, and the off-gas containing some SO_2 and SO_3 is recycled back to the converter-absorber.

CCC 69-31

H. Cost Estimates

TABLE X

CAPITAL INVESTMENT

1400 MW Power Plant, 0.2% SO_2 in Flue Gas
Production of Sulfuric Acid, 183,000 tons/yr

	Installed Equip. Cost*	Total Investment	Factor % of Total
Equipment			
Converter-absorber	$2,000,000		
Desorber and Separator	335,000		
Desorber blower	230,000		
Duct work and dampers	140,000		
Powder conveyors	130,000		
Flue gas exhauster	350,000		
Fines separator	120,000		
Sorb -cat. prep. facility	280,000		
Sorb -cat. storage	100,000		
Initial sorb -cat. charge	95,000		
SO_3 gas cooler	68,000		
SO_3 absorber	394,000		
Acid cooler	45,000		
Acid pumps and storage	146,000		
	$4,433,000	$4,433,000	43.44
Instruments		294,000	2.88
Electrical		196,000	1.92
Buildings		490,000	4.80
Yard Improvements		255,000	2.50
Utilities		785,000	7.69
Physical Plant Cost		6,453,000	63.23
Engineering and Constr.		1,293,000	12.68
Direct Plant Cost		7,746,000	75.91
Contractors fee		372,000	3.65
Contingency		1,160,000	11.34
Fixed Capital		9,278,000	90.90
Working Capital		942,000	9.10
Total Investment		$10,220,000	100.00

$10,220,000/1,400,000 KW = $7.30/KW

* Includes: Equipment, erection, foundations, piping, insulation

CCC 69-31

TABLE XI

CAPITAL INVESTMENT

1400 MW Power Plant, 0.2% SO_2 in Flue Gas
Concentration of SO_2 to 44 mole % Gas Stream

	Installed Equip. Cost*	Total Investment	Factor % of Total
Equipment			
Converter-absorber	$ 2,000,000		
Desorber and separator	170,000		
Desorber blower	40,000		
Duct work and dampers	140,000		
Powder conveyors	130,000		
Flue gas exhauster	350,000		
Fines separator	120,000		
Sorb.-cat. prep. facility	280,000		
Sorb.-cat. storage	100,000		
Initial sorb.-cat. charge	90,000		
	$ 3,420,000	$ 3,420,000	43.44
Instruments		227,000	2.88
Electrical		152,000	1.92
Buildings		378,000	4.80
Yard improvements		197,000	2.50
Utilities		606,000	7.69
Physical Plant Cost		4,980,000	63.23
Engineering and Constr.		1,000,000	12.68
Direct Plant Cost		5,980,000	75.91
Contractor fee		287,000	3.65
Contingency		895,000	11.34
Fixed Capital Cost		7,162,000	90.90
Working Capital		718,000	9.10
Total Investment		$ 7,880,000	100.00

$7,880,000/1,400,000 KW = $5.63/KW

* Includes: Equipment, erection, foundations, piping, insulation

CCC 69-31

TABLE XII

OPERATING COST

1400 MW Power Plant, 0.2% SO_2 in Flue Gas
330 Days/yr at 70% Capacity
Production of Sulfuric Acid, 183,000 tons/yr

		$/Year
Materials		
Make up sorb.-cat.:	6.5×10^6 lbs/yr x $0.0735/lb	478,000
Coal	4.08 tons/hr x 7920 x $4.00/ton	130,000
Utilities		
Power	9200 KW x 7920 x $0.006/KWH	437,000
Water	800 GPM x 60 x 7920 x $0.10/1000 gal.	38,000
Direct Labor		
3 men/shift:	72 hrs/day x 365 x $3.00	81,000
Supervision		12,000
Maintenance	5% Fixed Capital	464,000
Supplies	15% Maintenance	69,000
Payroll burden	20% labor and supervision	19,000
Plant overhead	50% labor + super. + maint. + supplies	313,000
Depreciation	10% Fixed Capital	928,000
Taxes	2% Fixed Capital	185,000
Insurance	1% Fixed Capital	93,000
Total Operating Cost		$3,247,000

$/ton coal = 3.25/3.21 = $1.01
mil/KWH = $3.25 \times 10^9 / 7.75 \times 10^9 = 0.42$

Breakeven acid sales price
$3,247,000/183,000 = $17.80/ton H_2SO_4

CCC 69-31

TABLE XIII

OPERATING COST

1400 MW Power Plant, 0.2% SO_2 in Flue Gas
330 Days/yr at 70% Capacity
Concentration of SO_2 to a 44% Gas Stream

		$/Year
Materials		
Make up sorb.-cat.:	6.5×10^6 lbs/yr x $0.0735/lb	478,000
Coal	2.31 tons/hr x 7920 x $4.00/ton	73,000
Utilities		
Power	8140 KW x 7920 x $0.006/KWH	387,000
Direct Labor		
2 man/shift	48 hrs/day x 365 x $3.00	53,000
Supervision		7,000
Maintenance	5% Fixed Capital	358,000
Supplies	15% Maintenance	53,800
Payroll Burden	20% labor and supervision	12,000
Plant Overhead	50% labor + super. + maint. + supplies	235,900
Depreciation	10% Fixed Capital	716,200
Taxes	2% Fixed Capital	143,200
Insurance	1% Fixed Capital	71,600
Total Operating Cost		$ 2,588,700

$/ton coal = 2.59/3.21 = $0.806/ton coal
Mil/KWH = $2.59 \times 10^8 / 7.75 \times 10^8 = 0.335$

IV. APPENDIX

TABLE XIV. EXPERIMENTAL DATA

Run No.	2A-1	2D-1	2A-2	2D-2	2A-3	2D-3	2A-4	3A-1	3D-1
Temperature, °C	330	330-605	330	550	330	550	330	375	550
Reactor diam., inches	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Particle size, mesh	3-8	3-8	3-8	3-8	3-8	3-8	3-8	3-8	3-8
Samples weight, grams	1.7396	1.7396	1.7396	1.7396	1.7396	1.7396	1.7396	1.7926	1.7926
Na_2SO_4, weight %	25	25	25	25	25	25	25	25	25
Gas flow, $cm^3/min.$	930	200	930	200	930	200	930	884	200
Oxygen flow, $cm^3/min.$	20		20		20		20	20	
SO_2 converter efficiency									
before, %	28		85		61		77	72	
after, %	30		76		89		49	69.5	
Gas composition (1)									
SO_2, ppm	2050		2050		2050		2050	2050	
SO_3									
H_2O									
NO_x									
Na_2SO_4 converted, %	56		66.7		84.6		89.9	26.8	
SO_3 recovered, %		92		104		96			94
Substrate	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2

TABLE XIV. EXPERIMENTAL DATA (continued)

Run No.	3A-2	3D-2	3A-3	3D-3	4A-1	4A-2	4D-2	4A-3a	4A-3b
Temperature, °C	375	550	330	500-550	300	300	550-600	375	325
Reactor diam., inches	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Particle size, mesh	3-8	3-8	3-8	3-8	3-8	3-8	3-8	3-8	3-8
Samples weight, grams	1.7926	1.7926	1.7926	1.7926	1.8533	1.8533	1.8533	1.8533	1.8533
Na_2SO_4, weight %	25	25	25	25	25	25	25	25	25
Gas flow, $cm^3/min.$	908	200	925	200	914	922	200	938	938
Oxygen flow, $cm^3/min.$	20		20		20	20		20	20
SO_2 converter efficiency									
before, %	70.5		63.6		73.5	62.8		54	54
after, %	68.4		89.0		72.3	82.0			
Gas composition (1)									
SO_2, ppm	2050		2050		2050	2050		2050	2050
SO_3									
H_2O									
NO_x									
Na_2SO_4 converted, %	15.6	173.6	80.8		36.7	58.6		8.1	49.1
SO_3 recovered, %				91.2			106		
Substrate	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2

TABLE XIV. EXPERIMENTAL DATA (continued)

Run No.	5A-1	5E-1[4]	6A-1	6A-2	6A-3	6A-4	6A-5	6E-4	6E-5
Temperature, °C	330	Varied	330	330	330	330	330	406-410	375
Reactor diam., inches	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Particle size, mesh	10-16	10-16	10-16	10-16	10-16	10-16	10-16	10-16	10-16
Samples weight, grams	0.4226(3)	0.4226(3)	0.4060	0.4060	0.4060	0.4060	0.4060	0.4060	0.4060
Na_2SO_4, weight %	25	25	25	25	25	25	25	25	25
Gas flow, cm^3/min.	930	930	930	930	1100	1100	1100	930	930
Oxygen flow, cm^3/min.	20	20	20	20	20	20	20	20	20
SO_2 converter efficiency									
before, %	74.5	74.5	51.5	81.9	77.3	89.8	63.2	83.9	63.2
after, %			79.2		89.8	83.9	97.8		97.8
Gas composition (1)									
SO_2, ppm	2050	2050	2050	2050	2050	2050	2050	2050	2050
SO_3									
H_2O, %					7	7	7		
NO_x									
Na_2SO_4 converted, %	80.6		85	93.1	103.6	107.7	103.9	19.3	30.6
SO_3 recovered, %									
Substrate	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2

TABLE XIV. EXPERIMENTAL DATA (continued)

Run No.	7A-1	7A-2	7A-3	7A-5	7A-6	8A-1	8D-1	8A-2	8D-2
Temperature, °C	300	300	300	300	330	330	550-585	330	550
Reactor diam., inches	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Particle size, mesh	10-16	10-16	10-16	10-16	10-16	10-16	10-16	10-16	10-16
Samples weight, grams	0.3913	0.3913	0.3913	0.3913	0.3913	0.645	0.645	0.645	0.645
Na_2SO_4, weight %	25	25	25	25	25	19.9	19.9	19.9	19.9
Gas flow, cm^3/min.	1100	930	1100	1100	1100	900	200	906	200
Oxygen flow, cm^3/min.	20	20	20	20	20	20		20	
SO_2 Converter efficiency									
before, %	88.8	81.6	123	67[8]	108[8]	96.4		104.8	
after, %	86.2	87.2		87[8]	63[8]	96.4		134.5	
Gas composition (1)									
SO_2, ppm	2050	2050	2050	3050	3050	3050		3050	
SO_3									
H_2O, %	7		7	7	7				
NO_x, ppm				500	500	500		500	
Na_2SO_4 converted, %	121	82.4	111	108	104	112.7		101.5	
SO_3 recovered, %							76.8		37.5
Substrate	SiO_2	SiO_2	SiO_2	SiO_2	SiO_2	Fly ash	Fly ash	Fly ash	Fly ash

TABLE XIV. EXPERIMENTAL DATA (continued)

Run No.	10A-1	10A-2	10A-3	10A-4
Temperature, °C	330	285	300	330
Reactor Diam., inches	0.25	0.25	0.25	0.25
Particle size, mesh	10-16	10-16	10-16	10-16
Samples weight, grams	0.400	0.400	0.400	0.400
Na_2SO_4, weight %	26.7	26.7	26.7	26.7
Gas flow, cm^3/min.	993	974	971	974
Oxygen flow, cm^3/min.	2	2	2	2
SO_2 Converter efficiency				
before, %	69	83	83	
after, %	91.6			67
Gas Composition (1)				
SO_2, ppm				
SO_3, ppm	210	225	211	225
H_2O				
NO_x				
Na_2SO_4 converted, %				
SO_3 recovered, %				
Substrate	SiO_2	SiO_2	SiO_2	SiO_2

TABLE XIV. EXPERIMENTAL DATA (continued)

Run 2A-1		Run 2D-1			Run 2A-2		Run 2D-2			Run 2A-3	
Time minutes	Balance Readings grams	Time minutes	Balance Readings grams	Temp. °C	Time minutes	Balance Readings grams	Time minutes	Balance Readings grams	Temp. °C	Time minutes	Balance Readings grams
0	8.4470	0	8.5835	330	0	8.4113	0	8.5895	RT	0	8.4475
6	8.4572	5	8.5761	445	5	8.4266	15	8.5897	200	5	8.4675
10	8.4708	10	8.5000	570	10	8.4437	20	8.5845	405	10	8.4875
15	8.4865	13	8.4798	585	15	8.4539	27	8.5670	510	15	8.5050
20	8.4927	16	8.4775	590	20	8.4603	31	8.5560	530	20	8.5165
25	8.5105	19	8.4697	600	25	8.4660	N_2 Started			25	8.5270
30	8.5158	22	8.4675		30	8.4719	35	8.5040	545	30	8.5345
35	8.5232	25	8.4660		35	8.4768	40	8.4400	555	40	8.5455
40	8.5286	30	8.4630		40	8.4825	45	8.4355	550	50	8.5536
45	8.5335	40	8.4540		45	8.4865	50	8.4335		60	8.5555
50	8.5374	50	8.4530		50	8.4905	55	8.4310		70	8.5588
55	8.5418	65	8.4560		55	8.4990	60	8.4290		80(2)	8.5588
60	8.5462	82	8.4530		65	8.5040	70	8.4265		90	8.5768
65	8.5490	95	8.4530		75	8.5110	80	8.4250		100	8.5910
70	8.5519	110	8.4525		100	8.5230	90	8.4228		110	8.6061
80	8.5558				130	8.5352	100	8.4210		130	8.6240
90	8.5655				160	8.5458	120	8.4195		160	8.6435
100	8.5699				190	8.5549				190	8.6550
110	8.5735				220	8.5625					
120	8.5745				250	8.5692					
130	8.5770				280	8.5748					
140	8.5775										
150	8.5735										

TABLE XIV. EXPERIMENTAL DATA (continued)

Run 2D-3			Run 2A-4		Run 3A-1		Run 3D-1		Run 3A-2	
Time minutes	Balance Readings grams	Temp. °C	Time minutes	Balance Readings grams	Time minutes	Balance Readings grams	Time minutes	Balance Readings grams	Time minutes	Balance Readings grams
0	8.6570	RT	0	8.4582	0	8.4980	0	8.5780	0	8.5011
23	8.6575	495	5	8.4730	5	8.5014	10	8.5900	5	8.5030
30	8.6255	525	10	8.4910	10	8.5060	20	8.5960	10	8.5060
35	8.6096	540	15	8.5072	20	8 5125	35	8.5650	15	8.5097
N_2 Started			20	8.5230	30	8 5140	53	8.5430	30	8.5315
38	8.4920	545	25	8.5378	40	8.5215	N_2 On		45	8.5349
41	8.4815	550	30	8.5505	50	8.5255	55	8.5360	75	8.5370
46	8.4774		35	8.5630	60	8.5300	59	8.5290	90	8.5400
50	8.4684		40	8.5732	70	8.5331	63	8.5250	105	8.5400
55	8.4699		50	8.5910	80	8.5360	68	8.5210	120	8.5405
65	8.4665		60	8.6072	90	8.5383	73	8.5160	135	8 5405
75	8.4635		70	8 6200	100	8.5410	83	8.5110		
85	8.4628		80	8.6305	120	8.5445	93	8.5095		
95	8.4620		90	8.6365	130	8.5455	103	8.5065		
105	8.4610		100	8.6490	140	8.5489	113	8.5055		
			120	8.6600	150	8 5500	143	8.5030		
			150	8.6693	170	8 5522	173	8.5020		
			180	8.6765	190	8.5541	203	8.5015		
			195	8.6779	210	8.5589	218	8.5020		
					240	8.5602				
					260	8.5645				
					280	8 5645				
					300	8.5655				

TABLE XIV. EXPERIMENTAL DATA (continued)

Run 3D-2			Run 3A-3		Run 3D-3			Run 4A-1		Run 4A-2	
Time minutes	Balance Readings grams	Temp. °C	Time Minutes	Balance Readings grams	Time minutes	Balance Readings grams	Temp. °C	Time minutes	Balance Readings grams	Time minutes	Balance Readings grams
0	8.5675	RT	0	8.4990	0	8.7028	330	0	8.5540	0	8.5467
30	8.5690	150	5	8.5042	15	8.6815	485	5	8.5560	2	8.5540
43	8.5520	365	10	8.5096		N_2 On		10	8.5565	4	8.5625
48	8.5390	485	15	8.5125	1	8.6490	500	15	8.5670	6	8.5725
60	8.5255	525	20	8.5143	2	8.6215	500	20	8.5715	8	8.5802
0	N_2 On	550	25	8.5195	3	8.6080	500	25	8.5760	10	8.5845
5	8.5165		30	8.5227	4	8.5855	500	37	8.5865	15	8.6000
10	8.5102		40	8.5490	5	8.5700	500	40	8.5885	25	8.6190
15	8.5080		50	8.5698	6	8.5660	500	50	8.5940	30	8.6255
20	8.5050		60	8.5780	7	8.5622	500	60	8.6000	40	8.6375
25	8.5035		70	8.5942	8	8.5550	500	70	8.6051	50	8.6472
30	8.5020		80	8.6035	9	8.5540	500	80	8.6076	60	8.6555
45	8.5000		110	8.6259	10	8.5521	500	90	8.6115	70	8.6610
			140	8.6582	15	8.5498	500	100	8.6140	80	8.6620
			170	8.6648	20	8.5481	500	110	8.6170	100	8.6780
			200	8.6749	25	8.5475	500	130	8.6225	120	8.6860
			230	8.6855	30	8.5460	500	160	8.6295	140	8.6923
			260	8.6934	45	8.5429	500	190	8.6365	160	8.7000
			290	8.7000	55	8.5415	500	210	8.6401		
			305	8.7028	65	8.5395	500	230	8.6460		
					70	8.5378	550	250	8.6500		
					75	8.5343	550				
					85	8.5289	550				
					95	8.5245	550				
					105	8.5225	550				
					125	8.5172	550				

TABLE XIV. EXPERIMENTAL DATA (continued)

Run 4D-2			Run 4A-3a		Run 4A-3b		Run 5A-1		Run 5E-1 (4)		
Time minutes	Balance Readings grams	Temp. °C	Time minutes	Balance Readings grams	Time minutes	Balance Readings grams	Time minutes	Balance Readings grams	Time minutes	Balance Readings grams	Temp. °C
0	8.7105	RT	0	8.5110	0	8.5300	0	0.0805	55	0.1285	330
10	8.7095	160	5	8.5198	5	8.5414	1	0.0825	60	0.1170	392
15	8.6100	335	10	8.5250	11	8.5580	2	0.0835	65	0.1120	400
20	8.6965	450	16	8.5270	15	8.5691	3	0.0868	70	0.1080	407
25	8.6740	510	20	8.5282	20	8.5825	4	0.0898	75	0.1045	405
30	8.6450	550	30	8.5300	25	8.5940	6	0.0950	80	0.1040	408
0	N_2 On	550	40	8.5321	30	8.6040	8	0.1010	85	0.1028	405
1	8.5900	550	50	8.5322	35	8.6150	10	0.1055	95	0.1010	410
2	8.5825	550	60	8.5322	40	8.6250	12	0.1095	105	0.0985	405
3	8.5805	550	70	8.5323	45	8.6343	14	0.1135	115	0.0985	405
5	8.5765	550			50	8.6420	16	0.1170	135	0.0986	409
10	8.5700	550			60	8.6585	20	0.1230	145	0.0965	440
15	8.5635	550					24	0.1265	155	0.0950	440
20	8.5605	550					26	0.1275	165	0.0935	440
25	8.5594	550					28	0.1285	175	0.0926	440
30	8.5585	550					30(3)	0.1245	185	0.0920	440
50	8.5525	550					40	0.1275	195	0.0920	440
70	8.5505	550					50	0.1285	205	0.0920	440
90	8.5525	550					55	0.1285	220	0.0550	615
100	8.5500	605									
120	8.5490	605									
130	8.5475	605									
150	8.5475	605									

TABLE XIV. EXPERIMENTAL DATA (continued)

Run 6A-1		Run 6A-2		Run 6A-3		Run 6A-4		Run 6A-5	
Time minutes	Balance Readings grams	Time minutes	Balance Readings grams	Time minutes	Balance Readings grams	Time minutes	Balance Readings grams	Time minutes	Balance Readings grams
0	0.1120	0	0.1045	0	0.1112	0	0.1095	0	0.1085
2	0.1155	2	0.1075	1 (5)	0.1110	5	0.1135	5	0.1190
4	0.1195	4	0.1130	3 (5)	0.1110	10	0.1325	10	0.1320
6	0.1240	6	0.1186	5 (5)	0.1100	15	0.1495	15	0.1395
8	0.1292	8	0.1226	10	0.1290	21	0.1580	20	0.1495
10	0.1343	10	0.1271	20	0.1380	25	0.1635	25	0.1585
12	0.1395	12	0.1325	30	0.1555	30	0.1670	30	0.1635
14	0.1431	14	0.1365	40	0.1670	35	0.1690	35	0.1660
16	0.1460	16	0.1405	50	0.1700	40	0.1695	40	0.1670
18	0.1485	18	0.1431	60	0.1705	50	0.1700	45	0.1680
20	0.1512	20	0.1455			60	0.1710	50	0.1678
24	0.1545	24	0.1490			70	0.1710	55	0.1680
30	0.1572	30	0.1519						
35	0.1590	35	0.1535						
40	0.1595	40	0.1550						
50	0.1605	50	0.1575						
55	0.1606	60	0.1578						

TABLE XIV. EXPERIMENTAL DATA (continued)

Run 6E-4 (6)			Run 6E-5 (7)			Run 7A-1		Run 7A-2		Run 7A-3	
Time minutes	Balance Readings grams	Temp. °C	Time minutes	Balance Readings grams	Temp. °C	Time minutes	Balance Readings grams	Time minutes	Balance Readings grams	Time minutes	Balance Readings grams
0	0.1710	330	0	0.1680	330	0	0.0996	0	0.0905	0	0.0982
5	0.1635	360	5	0.1654	350	1	0.1000	2	0.0948	2	0.0964
10	0.1470	395	10	0.1605	373	3	0.1096	4	0.1000	4	0.1040
15	0.1292	408	15	0.1520	375	5	0.1205	6	0.1032	6	0.1083
20	0.1230	408	20	0.1450	375	6	0.1295	8	0.1060	8	0.1146
25	0.1227	408	25	0.1370	375	8	0.1355	10	0.1080	10	0.1190
30	0.1210	408	30	0.1325	375	10	0.1420	12	0.1096	12	0.1215
35	0.1210	408	35	0.1300	375	15	0.1535	14	0.1115	14	0.1250
40	0.1205	408	40	0.1200	375	20	0.1640	16	0.1130	16	0.1288
45	0.1205	408	45	0.1265	375	25	0.1655	20	0.1151	18	0.1322
			50	0.1260	375	30	0.1665	30	0.1192	20	0.1360
			55	0.1260	375	35	0.1665	40	0.1225	25	0.1415
							H_2O Off	50	0.1250	30	0.1533
						40	0.1618	60	0.1274	35	0.1582
						45	0.1617	80	0.1298	40	0.1595
						50	0.1615	120	0.1325	50	0.1595
						65	0.1610	180	0.1359		H_2 Off
						95	0.1605			55	0.1555
							H_2O On			60	0.1555
						100	0.1660				
						105	0.1665				
							H_2O Off				
						110	0.1619				
						115	0.1617				
						120	0.1615				
						135	0.1614				

TABLE XIV. EXPERIMENTAL DATA (continued)

Run 7A-5		Run 7A-6		Run 8A-1		Run 8A-2		Run 8D-1		
Time minutes	Balance Readings grams	Time minutes	Balance Readings grams	Time minutes	Balance Readings grams	Time minutes	Balance Readings grams	Time minutes	Balance Readings grams	Temp. °C
0	0.0980	0	0.0960	0	0.3511	0	0.3675	0	0.4325	330
2	0.0985	2	0.1008	2	0.3585	2	0.3795		H_2O Off	
4	0.1120	4	0.1044	4	0.3700	5	0.3945	5	0.4305	330
6	0.1150	6	0.1181	6	0.3788	7	0.4050		N_2 On	
8	0.1180	8	0.1240	8	0.3855	9	0.4120	30	0.4100	550
10	0.1240	10	0.1400	12	0.4025	11	0.4175	45	0.3960	570
12	0.1280	12	0.1451	14	0.4093	15	0.4260	60	0.3900	565
14	0.1325	16	0.1500	16	0.4195	20	0.4300	90	0.3815	572
16	0.1390	18	0.1530	20	0.4232	25	0.4320	105	0.3795	570
20	0.1505	20	0.1540	25	0.4260	30	0.4337	120	0.3730	582
25	0.1575	25	0.1535	30	0.4295	35	0.4350	150	0.3720	585
30	0.1576	30	0.1535	35	0.4310	40	0.4365	180	0.3710	585
35	0.1575			40	0.4320	45	0.4370	210	0.3700	585
55	0.1575			45	0.4325	50	0.4375			
						60	0.4385			
						65	0.4410			

TABLE XIV. EXPERIMENTAL DATA (continued)

Run 8D-2			Run 10A-1		Run 10A-2		Run 10A-3			Run 10A-4	
Time minutes	Balance Readings grams	Temp. °C	Time minutes	Balance Readings grams	Time minutes	Balance Readings grams	Time minutes	Balance Readings grams	Temp. °C	Time minutes	Balance Readings grams
	SO_2 On										
0	0.4410	330	1	0.1235	0	0.1035	0	0.1030	300	0	0.1080
5	0.4394	330	6	0.1235	5	0.1062	5	0.1058	300	5	0.1070
10	0.4389	330	16	0.1238	10	0.1099	10	0.1082	300	10	0.1070
30	0.4360	330	21	0.1245	15	0.1114	15	0.1102	300	20	0.1080
	SO_2 Off		26	0.1245	20	0.1130	20	0.1106	300	30	0.1075
5	0.4360	365	31	0.1245	25	0.1140	25	0.1120	300	40	0.1070
10	0.4350	425	36	0.1250	30	0.1145	30	0.1130	300	50	0.1070
15	0.4340	455	41	0.1260	40	0.1161	35	0.1140	300	70	0.1080
25	0.4320	530	46	0.1273	50	0.1175	40	0.1146	300	85	0.1080
30	0.4320	545	51	0.1290	60	0.1188	50	0.1156	300		
	N_2 On		56	0.1292	70	0.1188	60	0.1170	300		
5	0.4275	555	61	0.1300	80	0.1200	70	0.1175	300		
10	0.4255	560	66	0.1300	90	0.1212	75	0.1184	300		
15	0.4250	558	71	0.1300			85	0.1183	330		
20	0.4225	554	76	0.1305			90	0.1172	330		
25	0.4215	553	81	0.1310			95	0.1164	330		
30	0.4205	555	86	0.1310			100	0.1160	330		
35	0.4180	555	91	0.1310			105	0.1157	330		
40	0.4168	555					110	0.1154	330		
50	0.4140	553					120	0.1153	330		
60	0.4115	555					130	0.1150	330		
70	0.4090	553					135	0.1149	330		
80	0.4085	553									
90	0.4085	553									

TABLE XIV. EXPERIMENTAL DATA (continued)

NOTES:

1. Gas consists of N_2 plus components indicated.
2. Oxygen flow to converter temporarily cut off.
3. At this point we appear to have lost a portion of sample by carry over in the gas. A plot gives estimate of 5 mg.
4. Continuation of 5A-1.
5. Problems with SO_2 value.
6. Continuation of 6A-4.
7. Continuation of 6A-5.
8. NO_x interferred with chemical analysis of trap solutions.
9. Low concentration SO_3 stream prepared by diluting with N_2 after converter.